1st Workshop on Pyrotechnic Combustion Mechanisms
Fort Collins, Colorado, USA
10th July 2004

Berger	Factors influencing the pyrotechnic reaction.
Dolata	Reassessment of the identity of the blue light emitter in copper-containing pyrotechnic flames.
Dreizin	Ignition of aluminium powders under different experimental conditions.
Granier	Ignition and combustion of nanocomposite Al/MoO_3.
Klapötke	Mechanistic studies concerning the hypergolic ignition between monomethylhydrazine (MMH) and dinitrogen tetroxide (NTO)
Klapötke	Synthesis, structure molecular orbital and valence bond calculations and decomposition mechanism for tetrazole azide CHN_7.
Koch	The HSAB-principle and its application to energetic materials and systems.
Sturman	Metal monochloride emitters in pyrotechnic flames – ions or neutrals?
Kosanke	Metal monochloride emitters in pyrotechnic flames – ions or neutrals?
Webb	Using thermodynamic codes to simulate pyrotechnic reactions.
Weiser	Fast emission spectroscopy for a better understanding of pyrotechnic combustion behaviour.

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FACTORS INFLUENCING the PYROTECHNIC REACTION

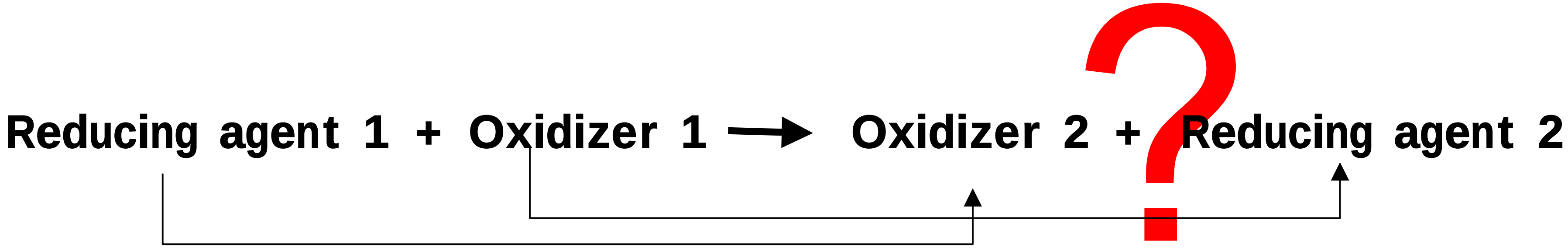
Beat Berger
Leader Energetic Material Research and Technology
Science and Technology Centre

Topics

- Pyrotechnic reaction
- Performance data / Determination
- Factors influencing the performance
- Summary / Future

Pyrotechnic Reaction

Redox reaction



Reducing agent 1 + Oxidizer 1 → Oxidizer 2 + Reducing agent 2

Performance Data of Pyrotechnics

- Reaction rate
- Heat of reaction
- Reaction temperature
- Reaction products
- Ignition temperature / Thermal stability
- Light emission

Determination of Pyrotechnic Data

Heat of Reaction

- Calculations with the EKVI or ICT Code
- Measurements in a adiabatic calorimeter

Determination of Pyrotechnic Data

Heat of Reaction

Determination of Pyrotechnic Data

Reaction Rate

- Calculations using the equation of Hill et al
- Measurements in a burning rinse
- Measurements in a tube

Determination of Pyrotechnic Data

Reaction Rate Calculated with the Equation of Hill et al

$$vB = k \times q / b \times c^2 \times \rho \times (T_i - T_a)$$

vB : Burning velocity [cm / s]

k : Heat transfer [cal / cm s °C]

q : Heat of reaction [cal / g]

b : Lengh of the reaction zone [cm]

c : Specific heat [cal / g °C]

ρ : Density [g / ccm]

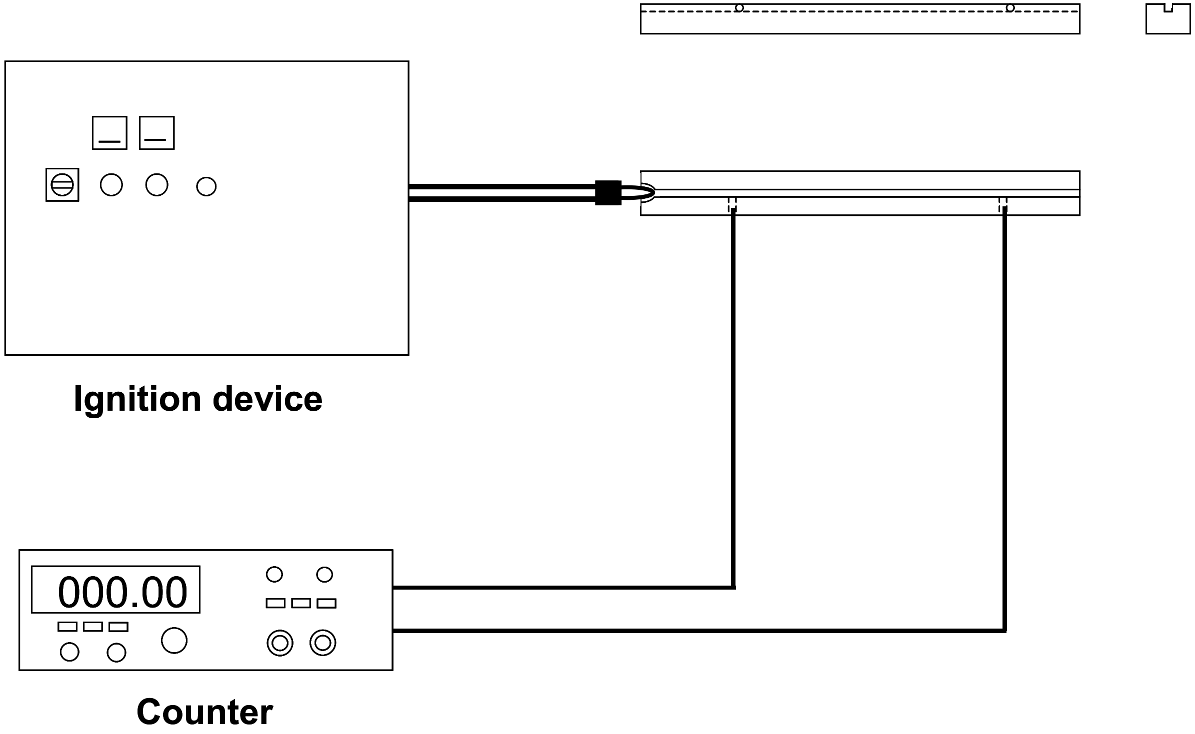
T_i : Burning temperature [°C]

T_a : Surrounding temperature [°C]

Determination of Pyrotechnic Data

Reaction Rate

Experimental Set Up



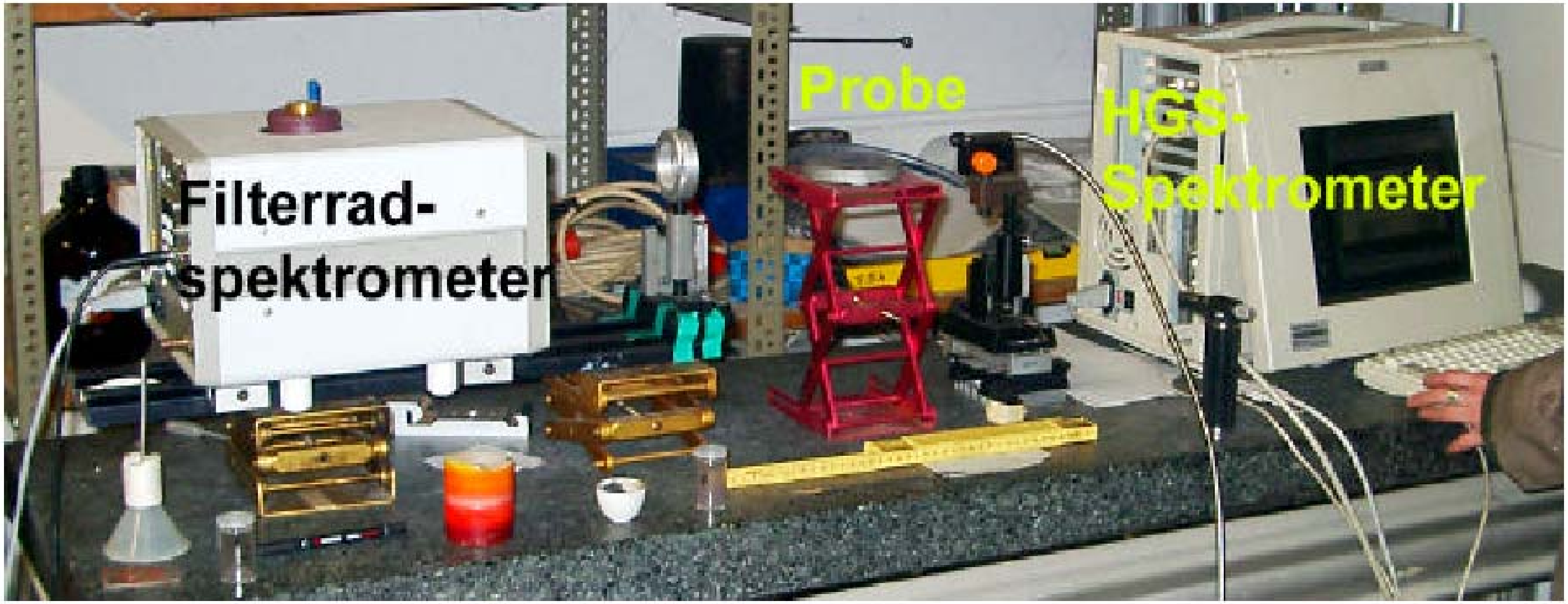
Determination of Pyrotechnic Data

Reaction Temperature

- Calculations with the EKVI or ICT Code
- Measurements with emission spectrometers

Determination of Pyrotechnic Data

Reaction Temperature



Determination of Pyrotechnic Data

Thermal Behaviour

- Thermal Gravimetry Analysis TGA
- Hot Stage Microscopy
- Differential Scanning Calorimetry DSC

Determination of Pyrotechnic Data

Reaction Products

- Calculations with the EKVI or ICT Code

- Measurements with TGA, MS and XRD

Factors Influencing the Pyrotechnic Reaction

- Type of reducing agent / oxidizer
- Purity / Oxide layer
- Particle size / specific surface
- Oxygen balance
- Binder type / binder content
- Mixing procedure

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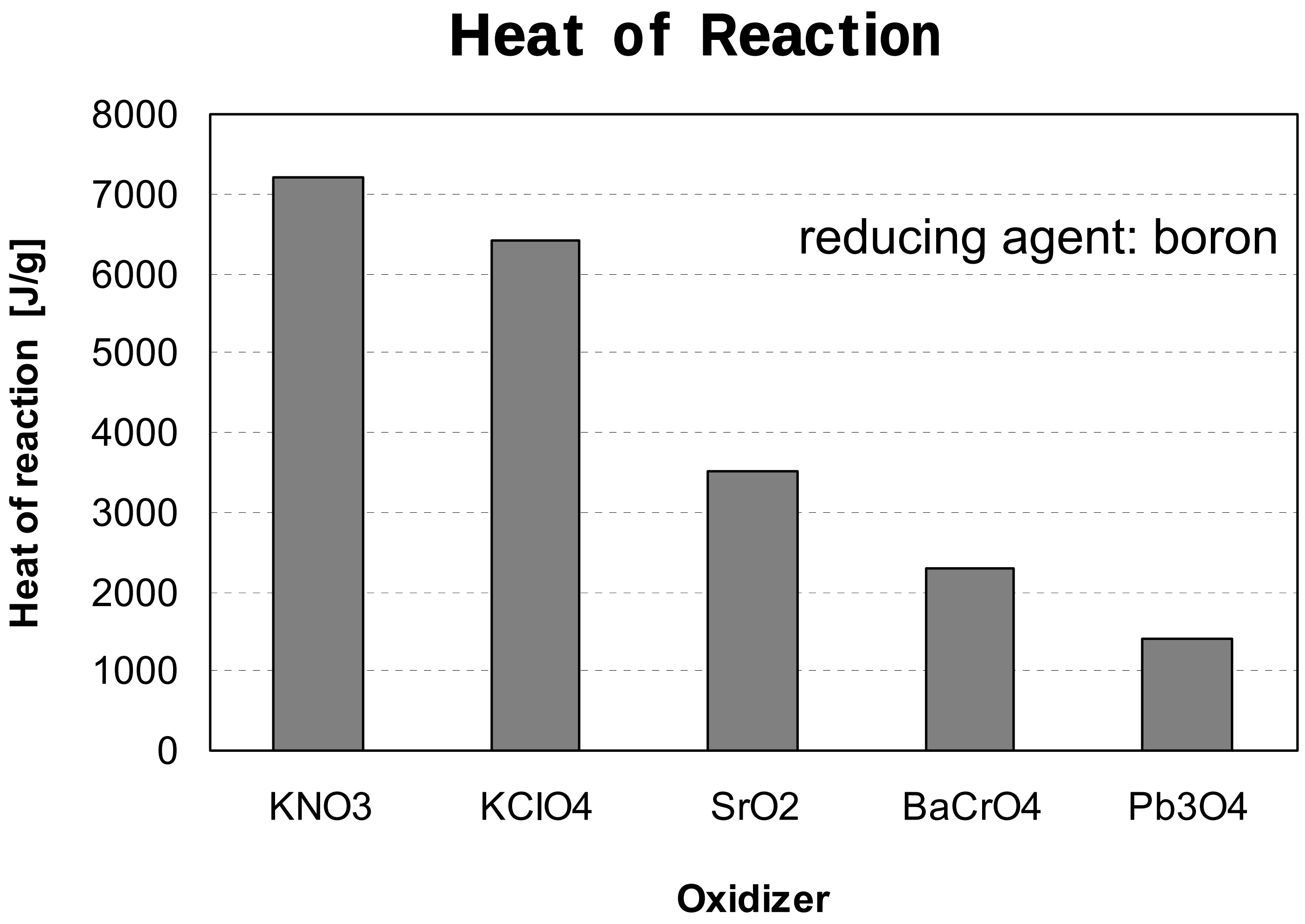
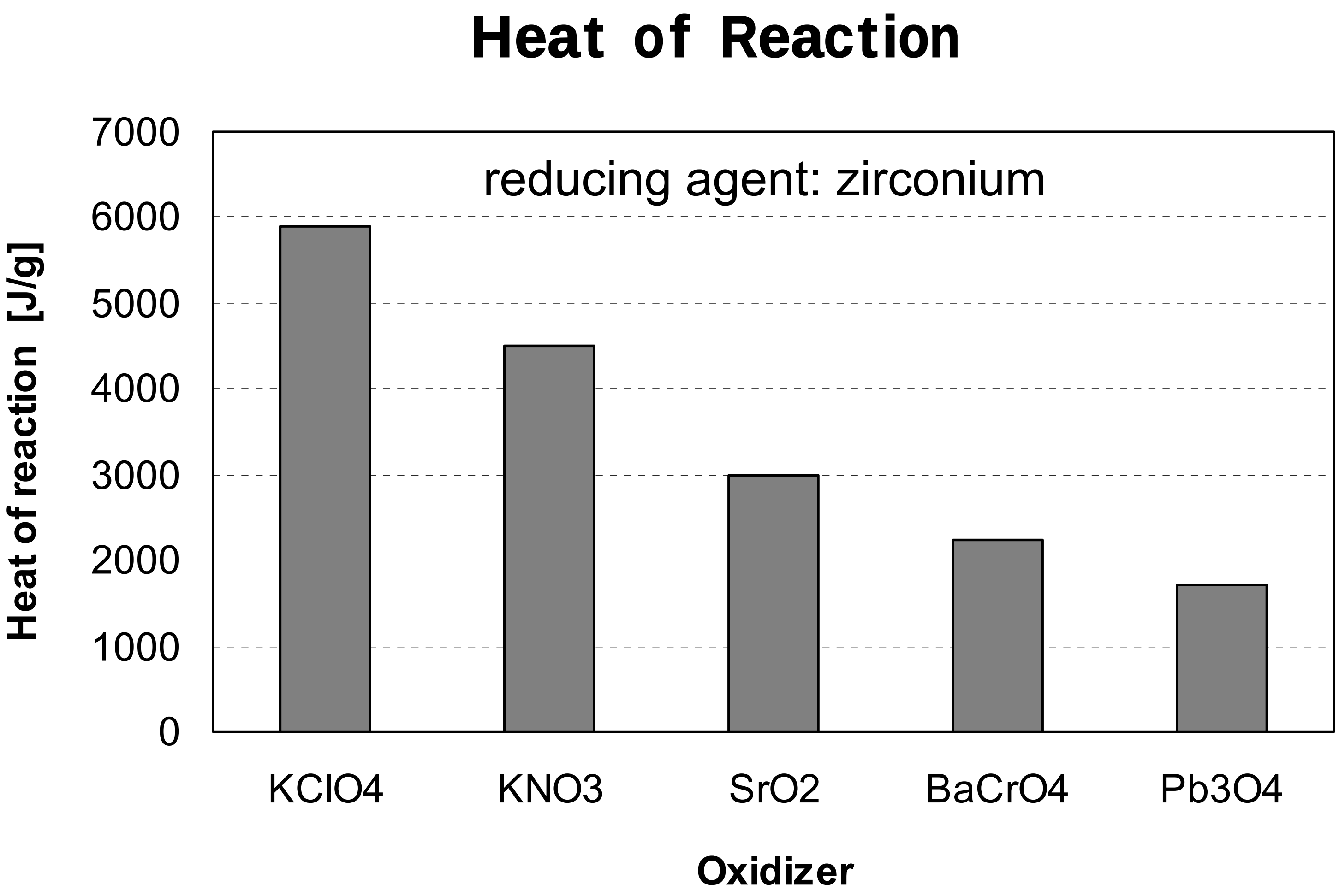
Type of Ingredient

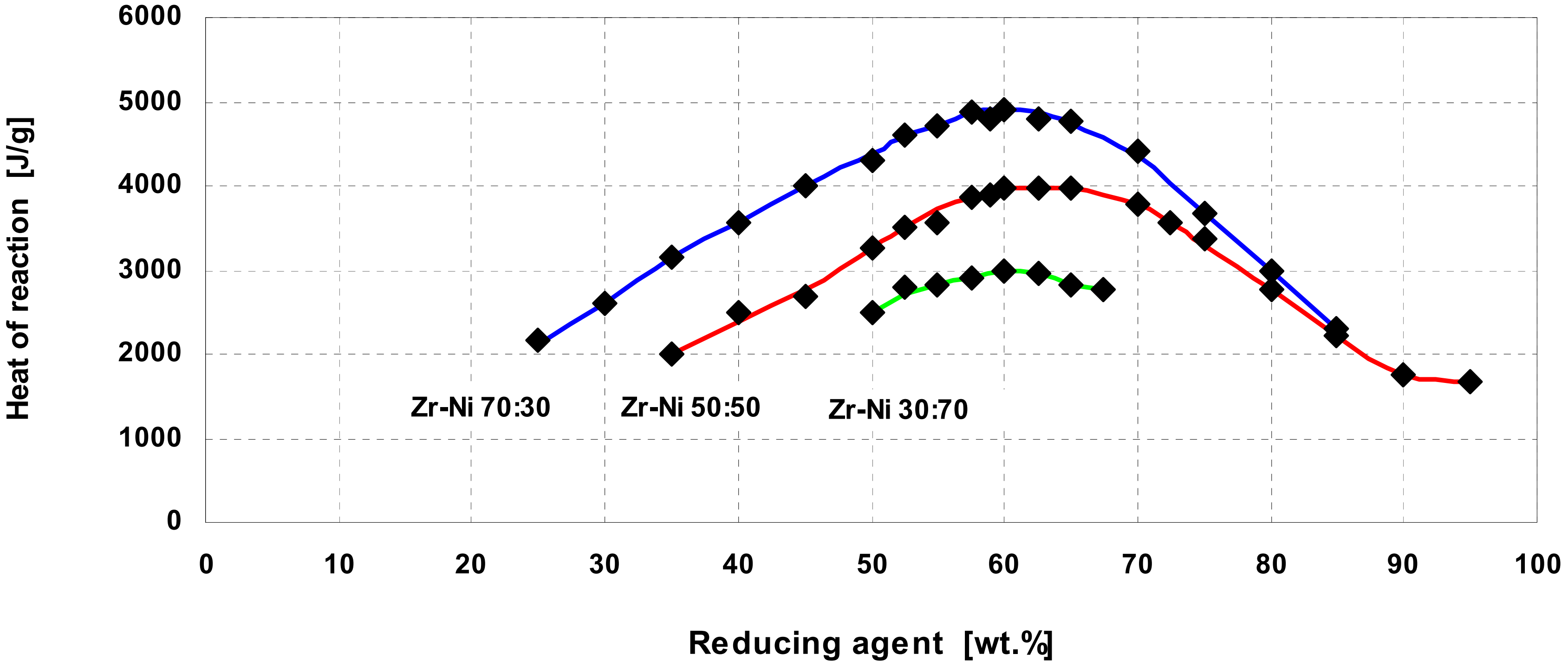


Type of Ingredient

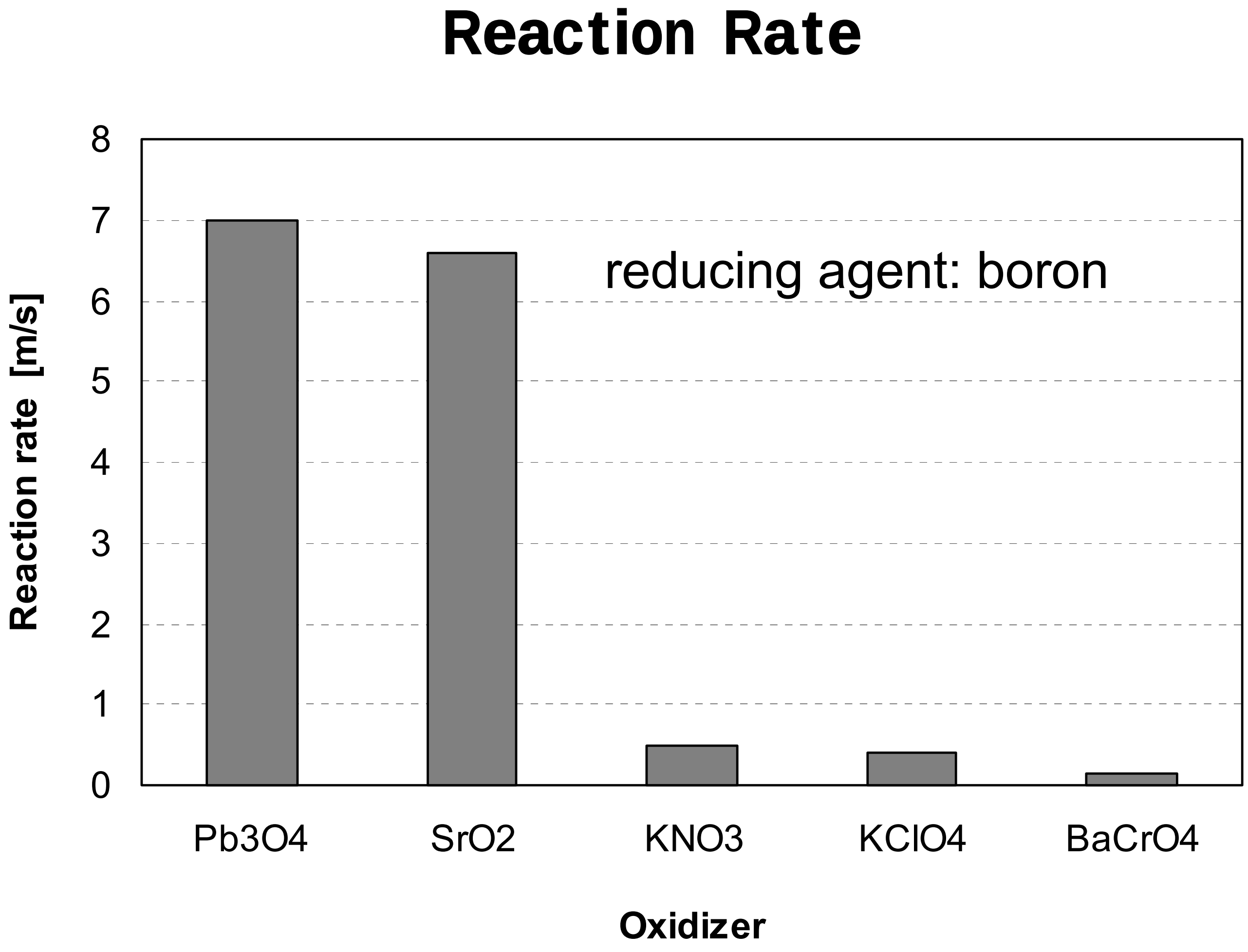


Type of Ingredient

Heat of Reaction



Type of Ingredient



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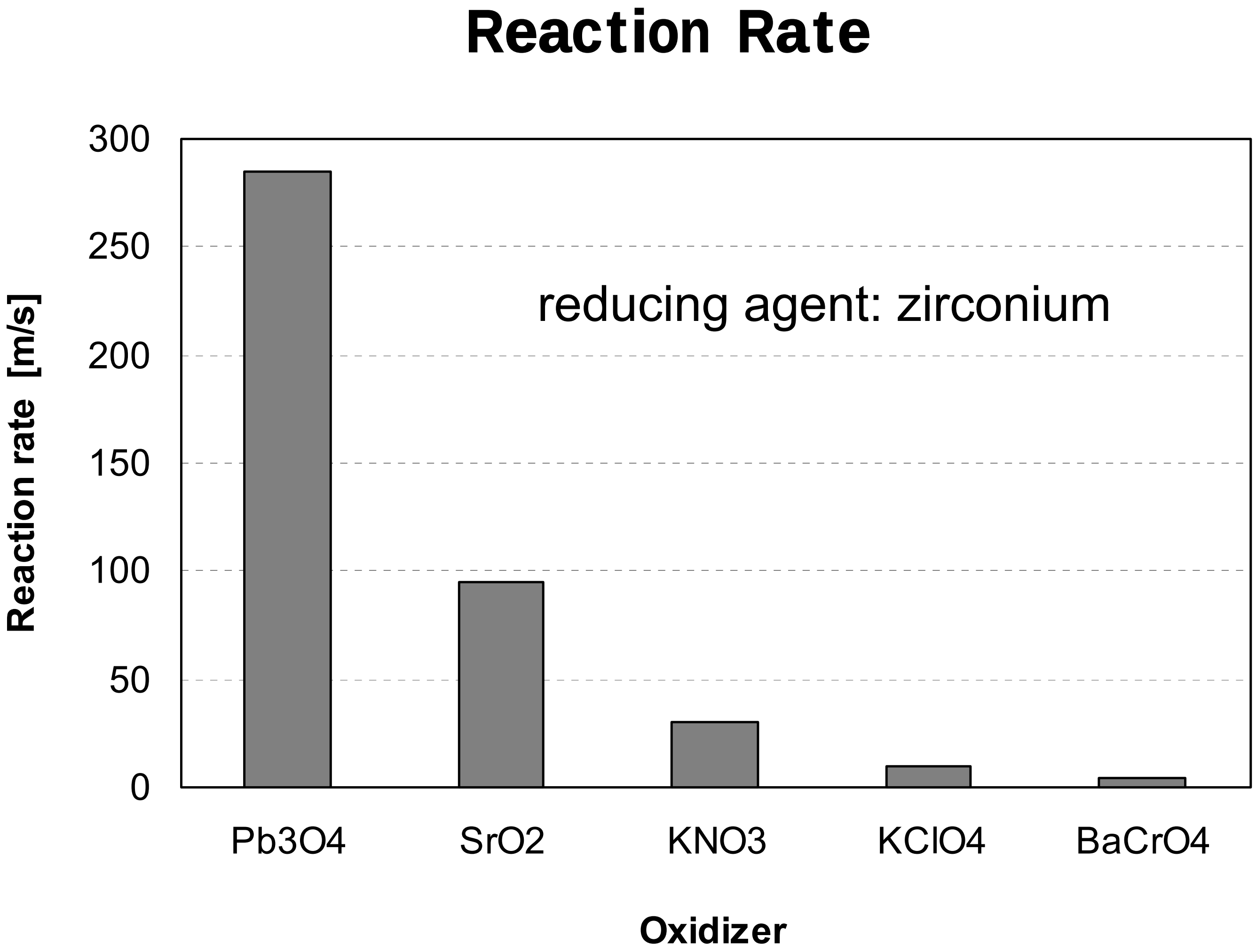
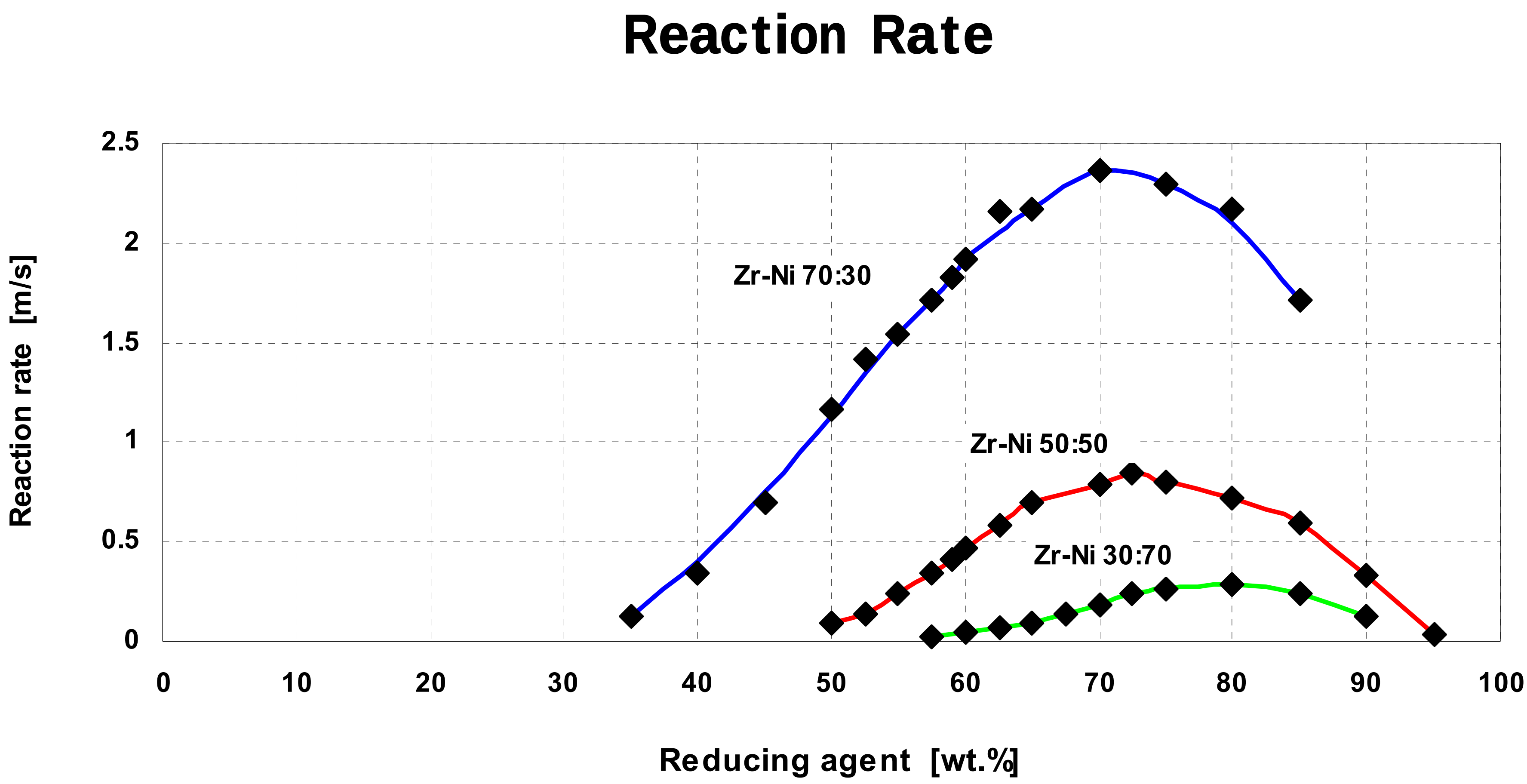
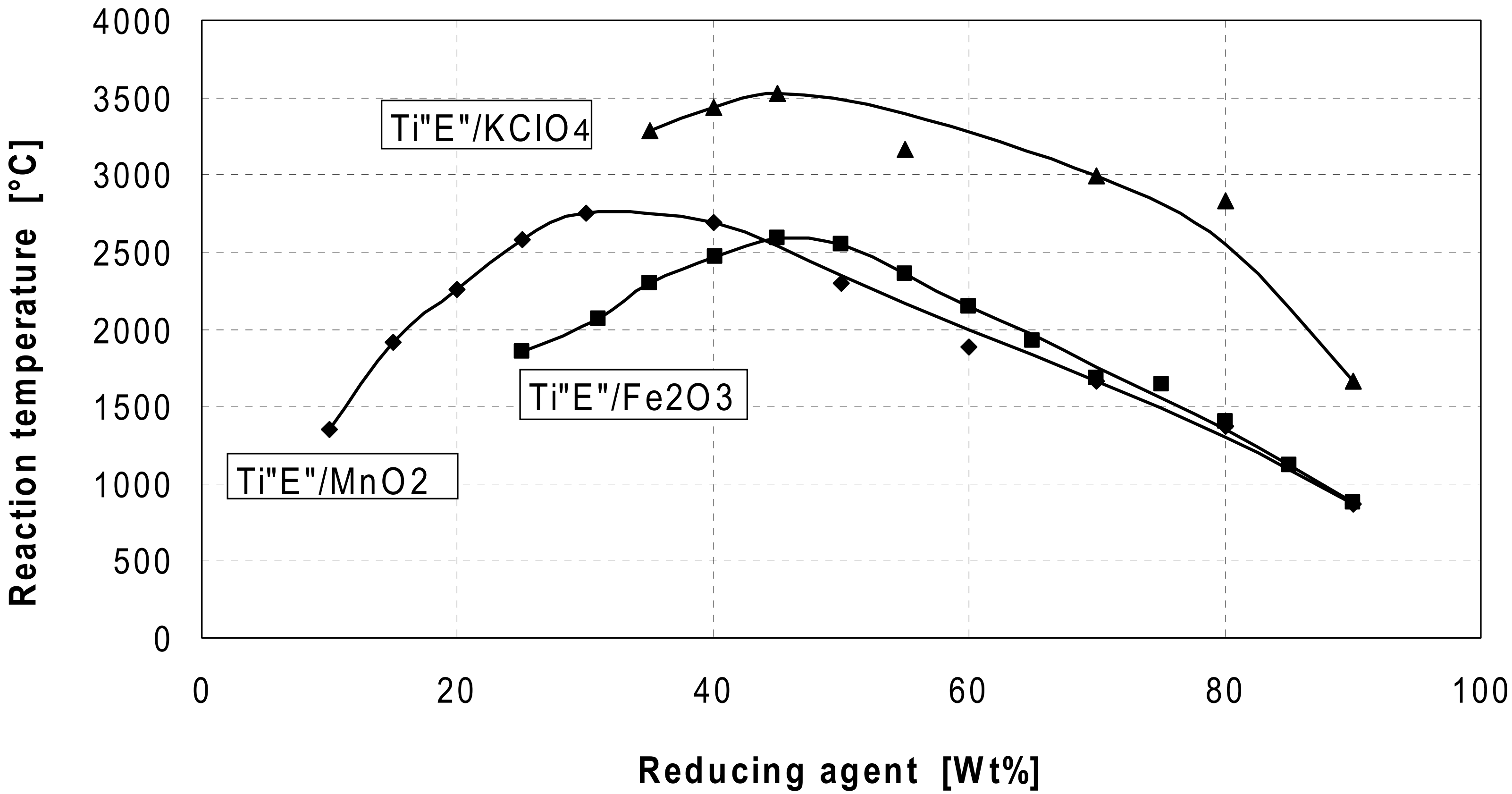


Type of Ingredient



Type of Ingredient

Reaction Temperature



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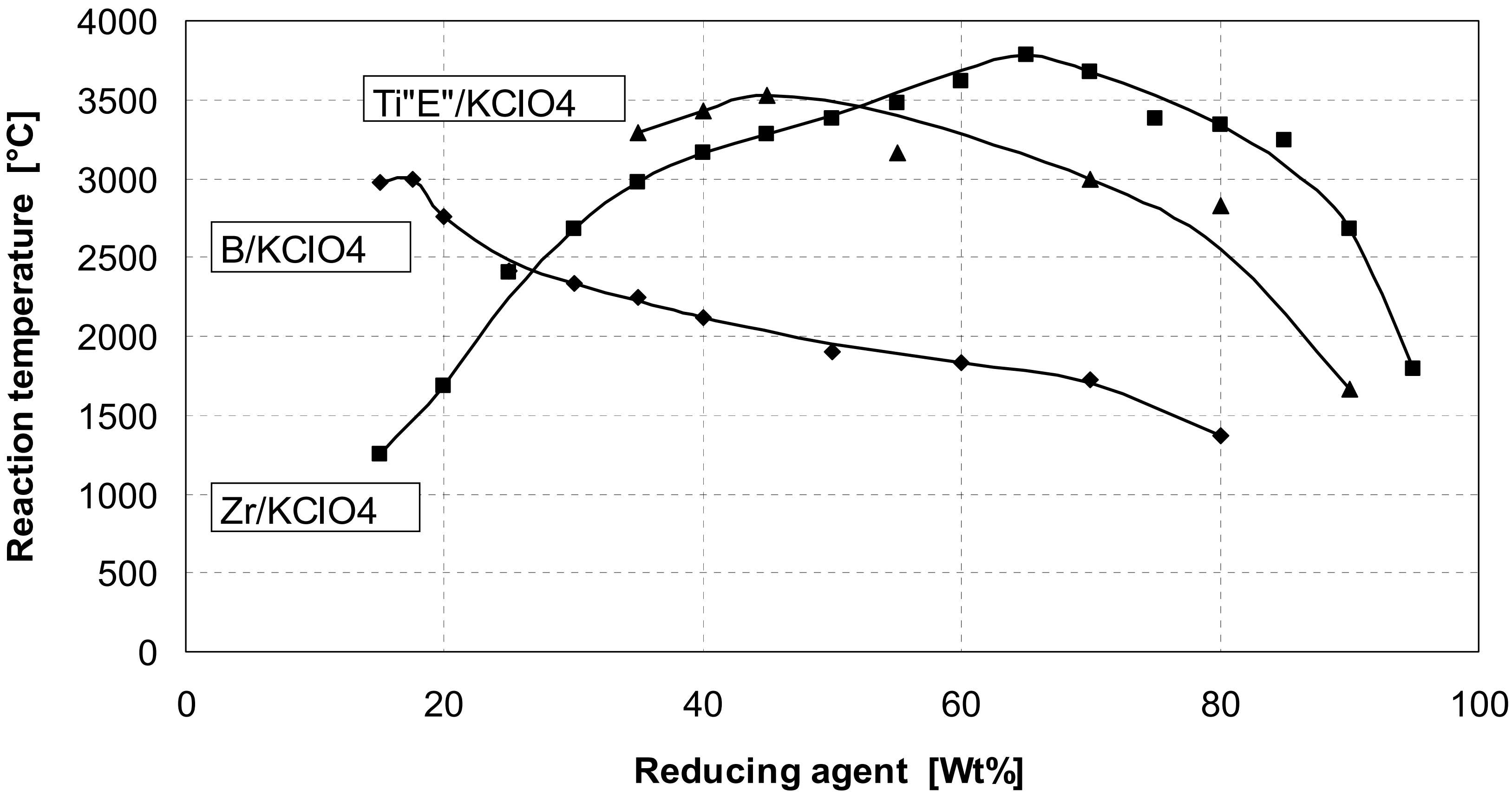
▪ Type of Ingredient

Reaction Temperature



Factors Influencing the Pyrotechnic Reaction

- Type of reducing agent / oxidizer
- Purity / Oxide layer
- Particle size / specific surface
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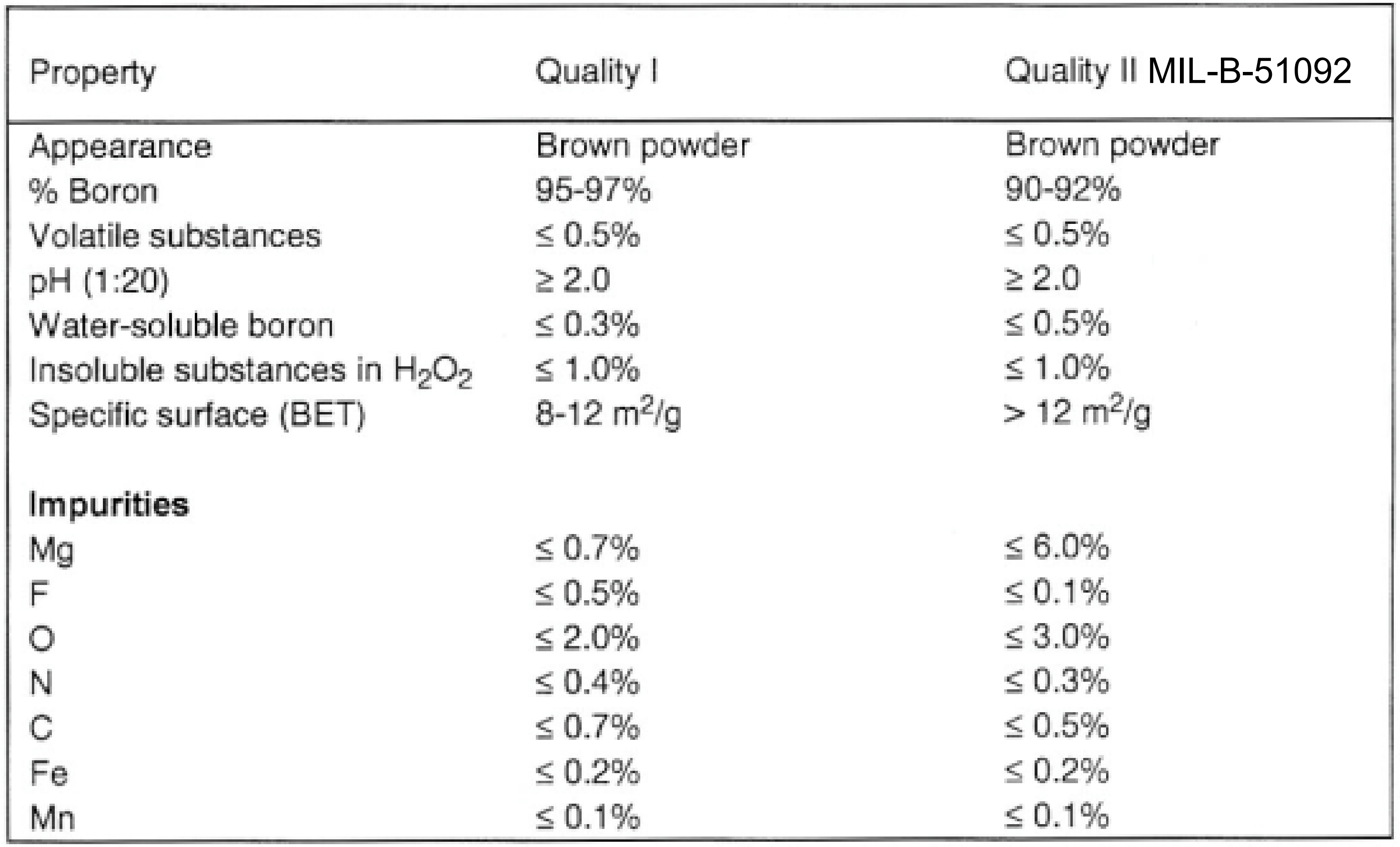
- Mixing procedure

Purity of Ingredients



Property	Quality I	Quality II MIL-B-51092
Appearance	Brown powder	Brown powder
% Boron	95-97%	90-92%
Volatile substances	≤ 0.5%	≤ 0.5%
pH (1:20)	≥ 2.0	≥ 2.0
Water-soluble boron	≤ 0.3%	≤ 0.5%
Insoluble substances in H_2O_2	≤ 1.0%	≤ 1.0%
Specific surface (BET)	8-12 m^2/g	> 12 m^2/g
Impurities		
Mg	≤ 0.7%	≤ 6.0%
F	≤ 0.5%	≤ 0.1%
O	≤ 2.0%	≤ 3.0%
N	≤ 0.4%	≤ 0.3%
C	≤ 0.7%	≤ 0.5%
Fe	≤ 0.2%	≤ 0.2%
Mn	≤ 0.1%	≤ 0.1%

Factors Influencing the Pyrotechnic Reaction

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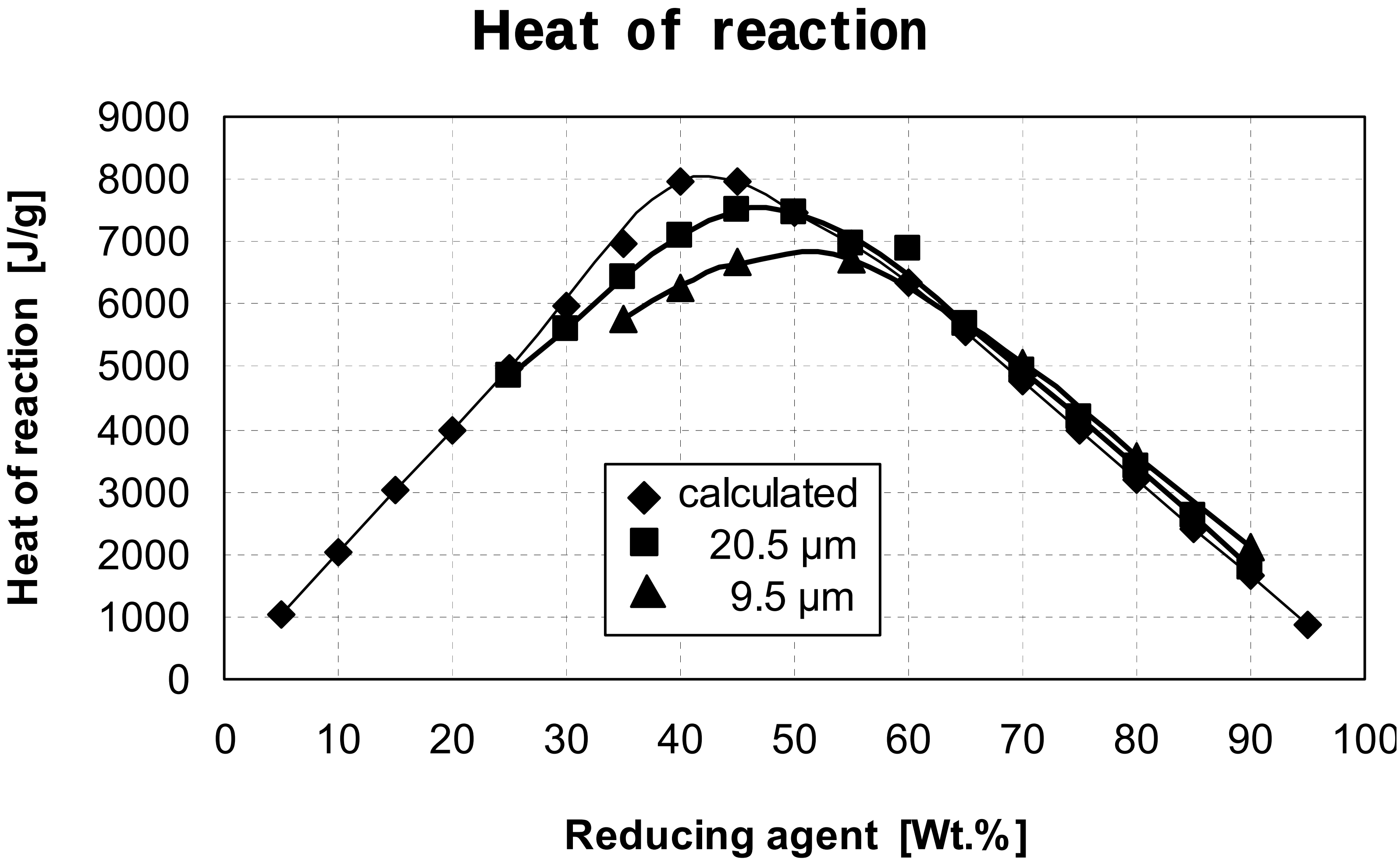
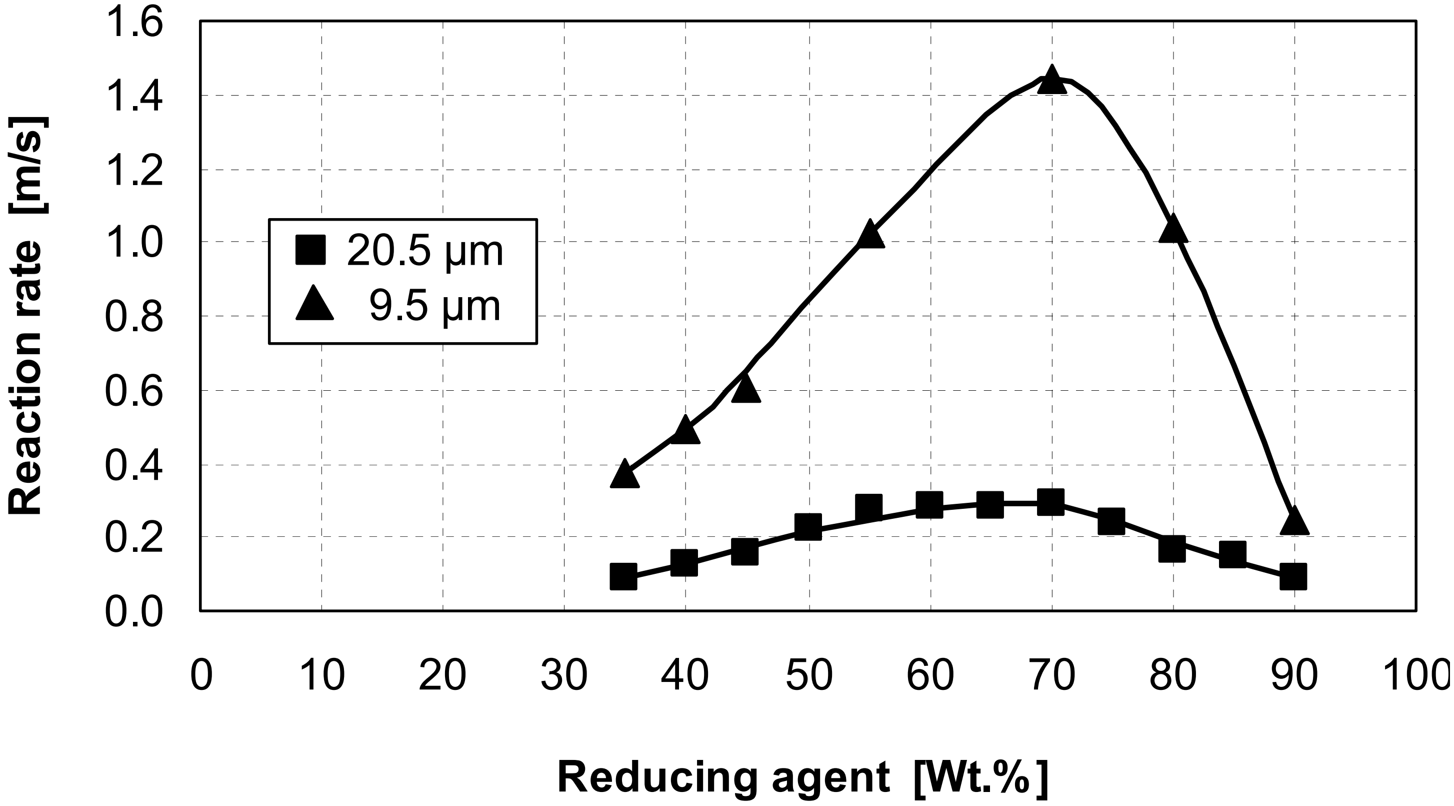
▪ Particle Size



Particle Size

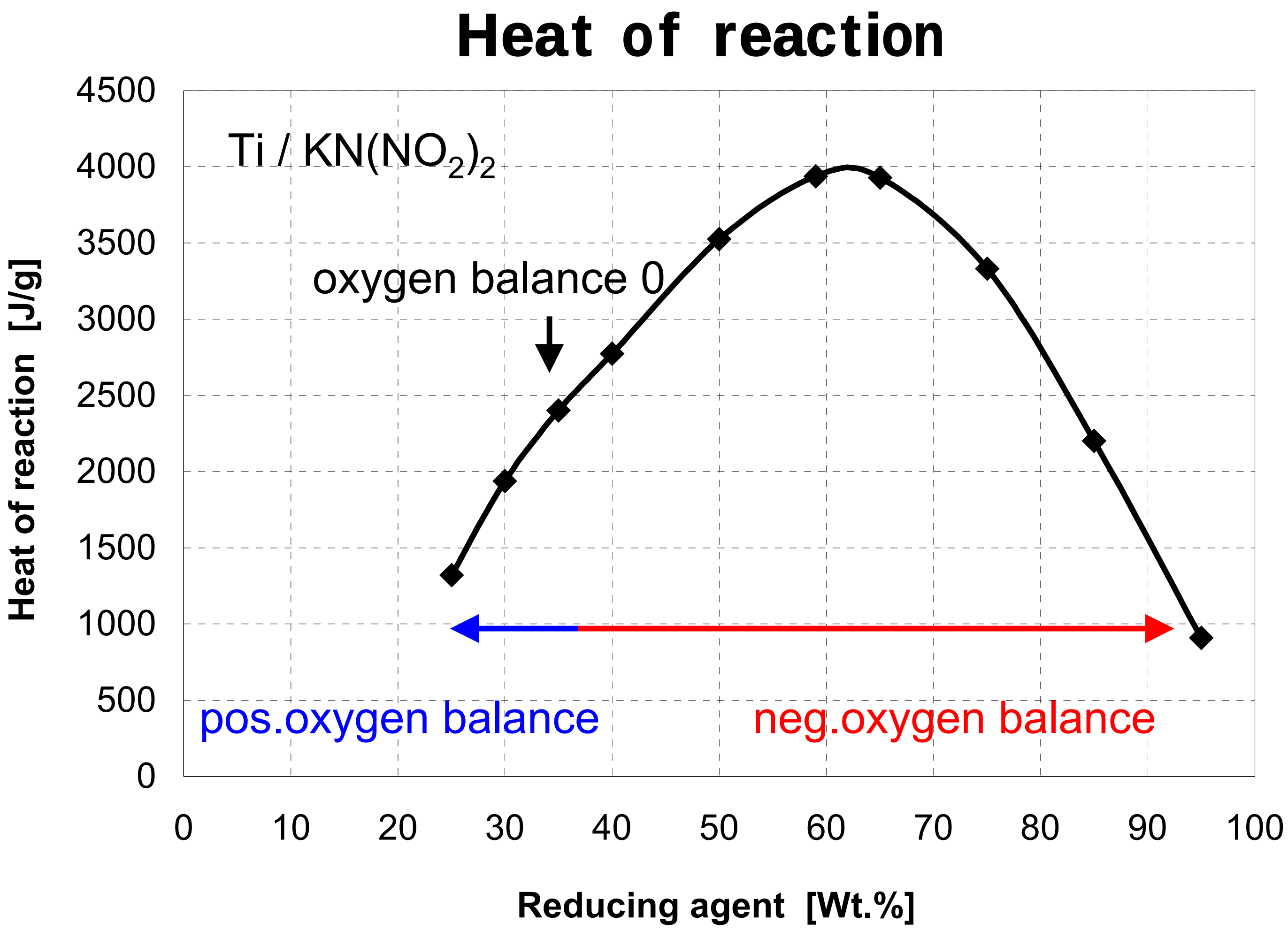
Reaction Rate



Factors Influencing the Pyrotechnic Reaction

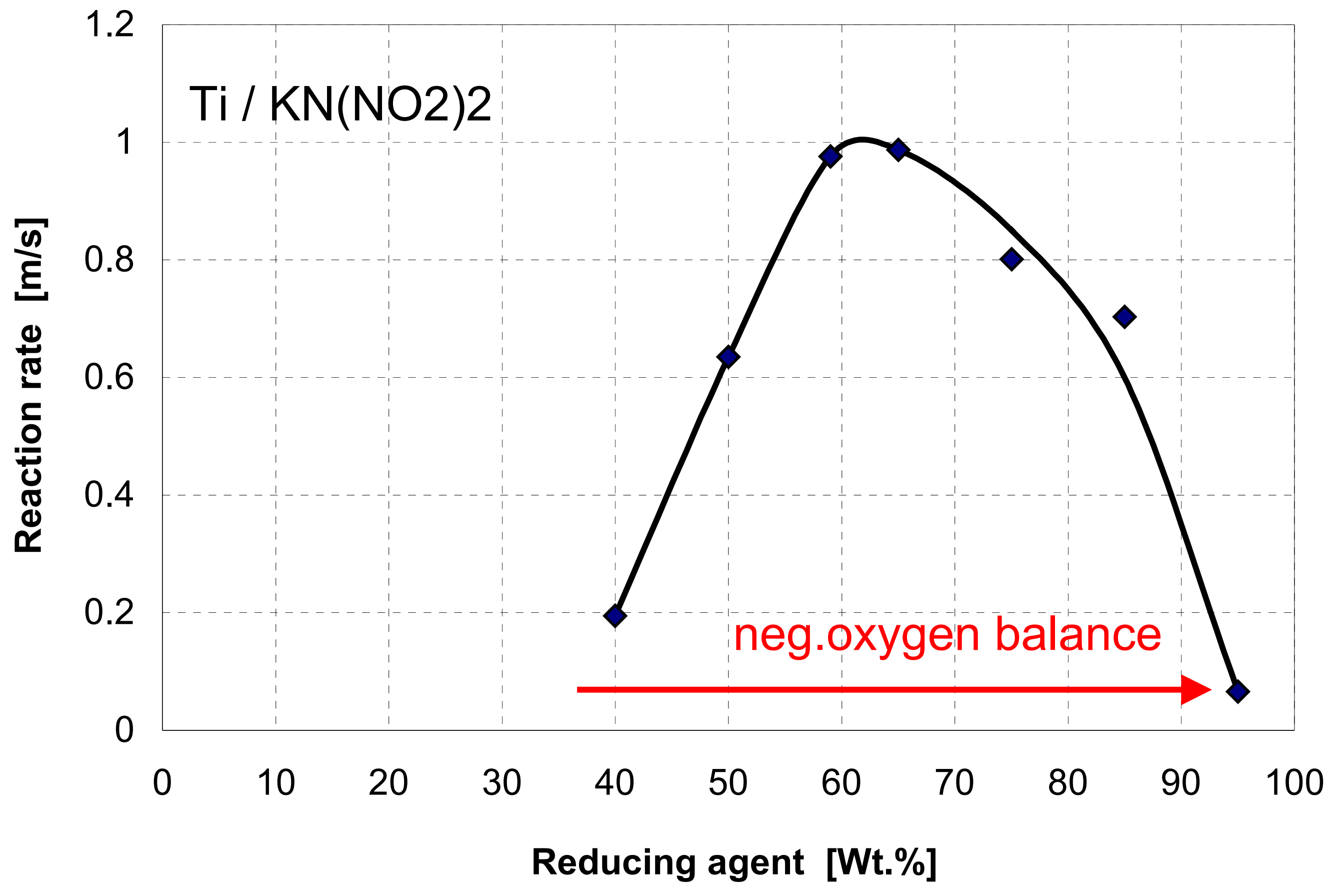
- Type of reducing agent / oxidizer
- Purity / Oxide layer
- Particle size / specific surface
- Oxygen balance
- Binder type / binder content
- Mixing procedure

Oxygen Balance



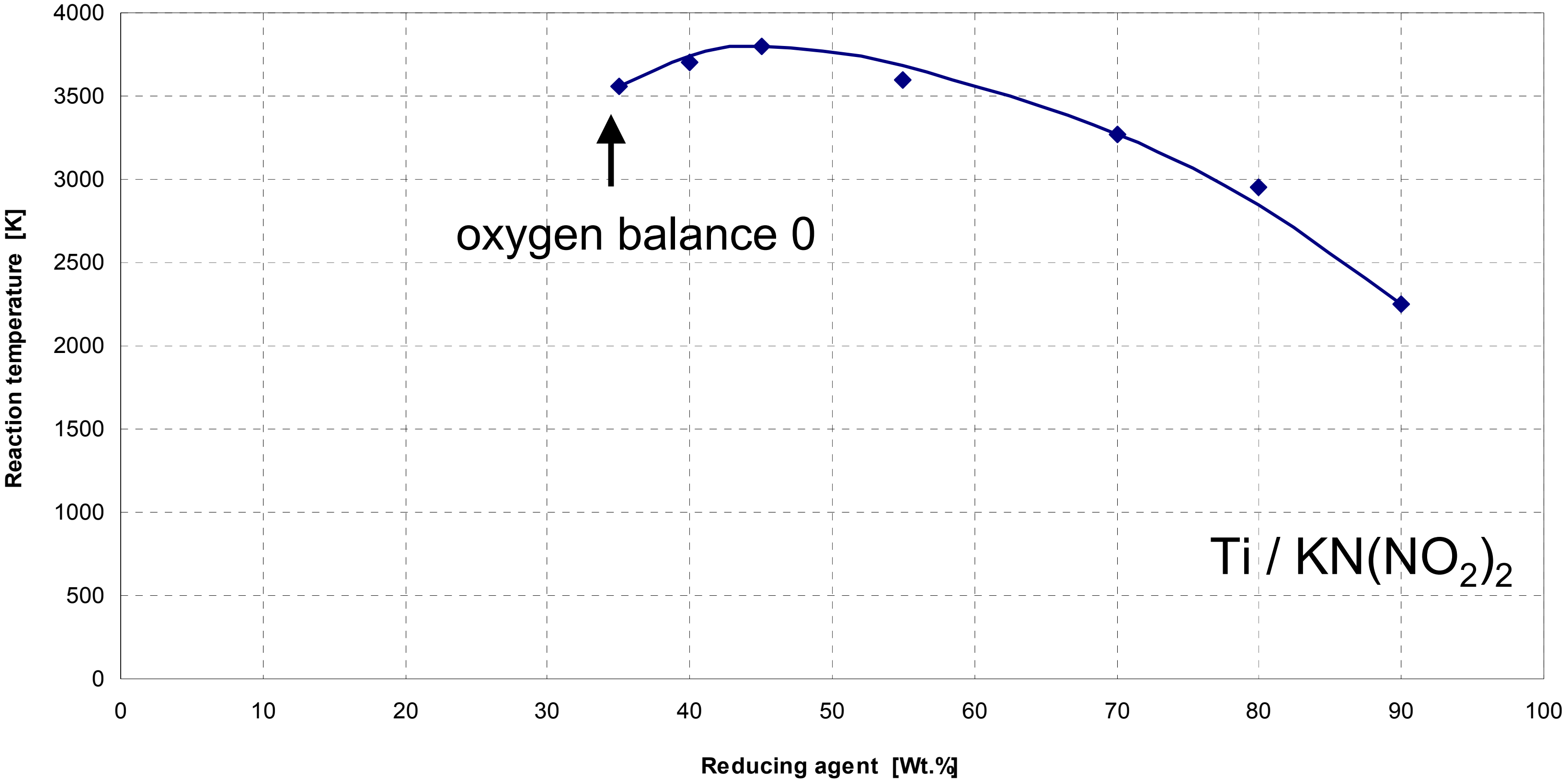
Oxygen Balance

Reaction Rate



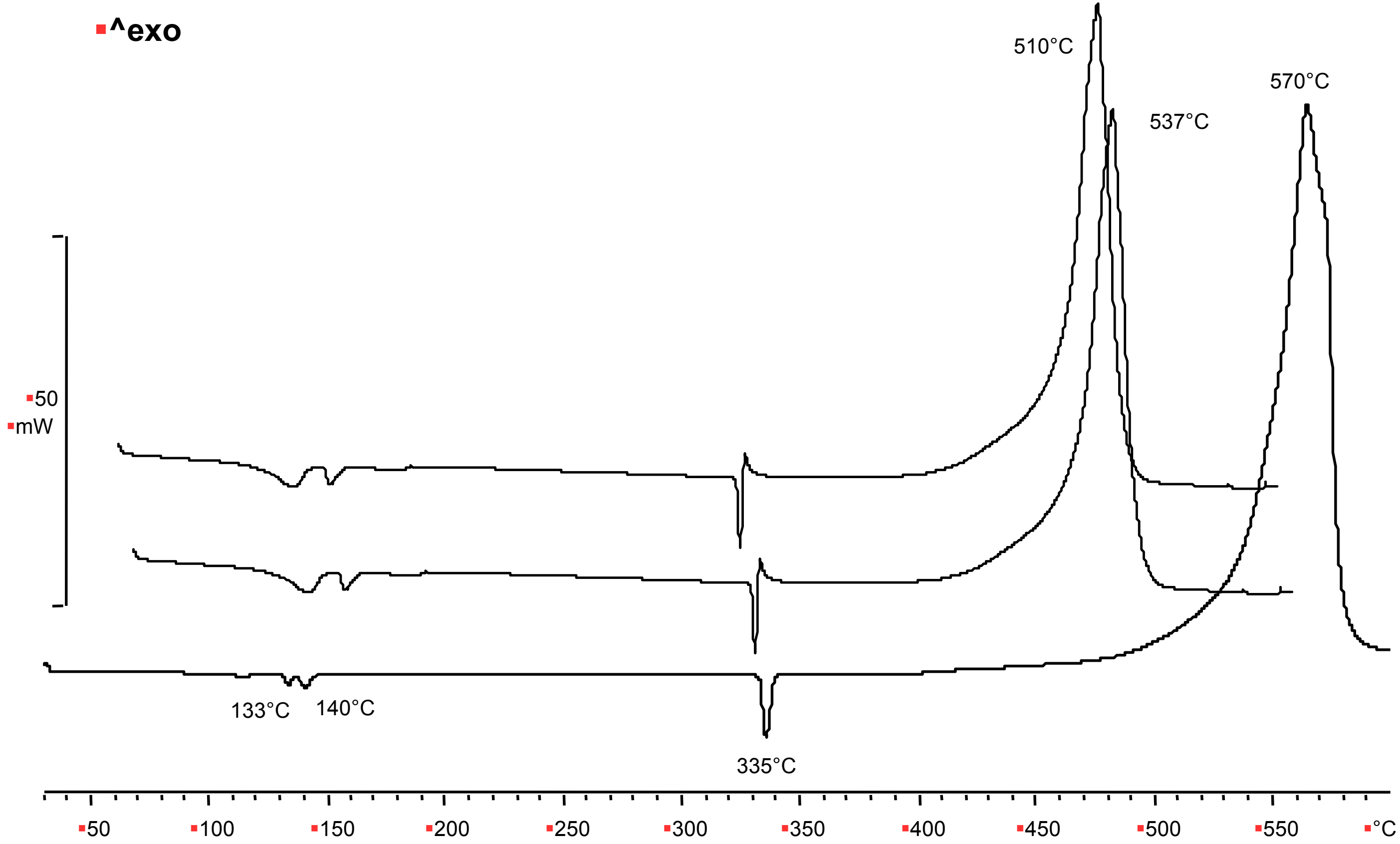
Oxygen Balance

Reaction Temperatur



Oxygen Balance

Termal Behaviour

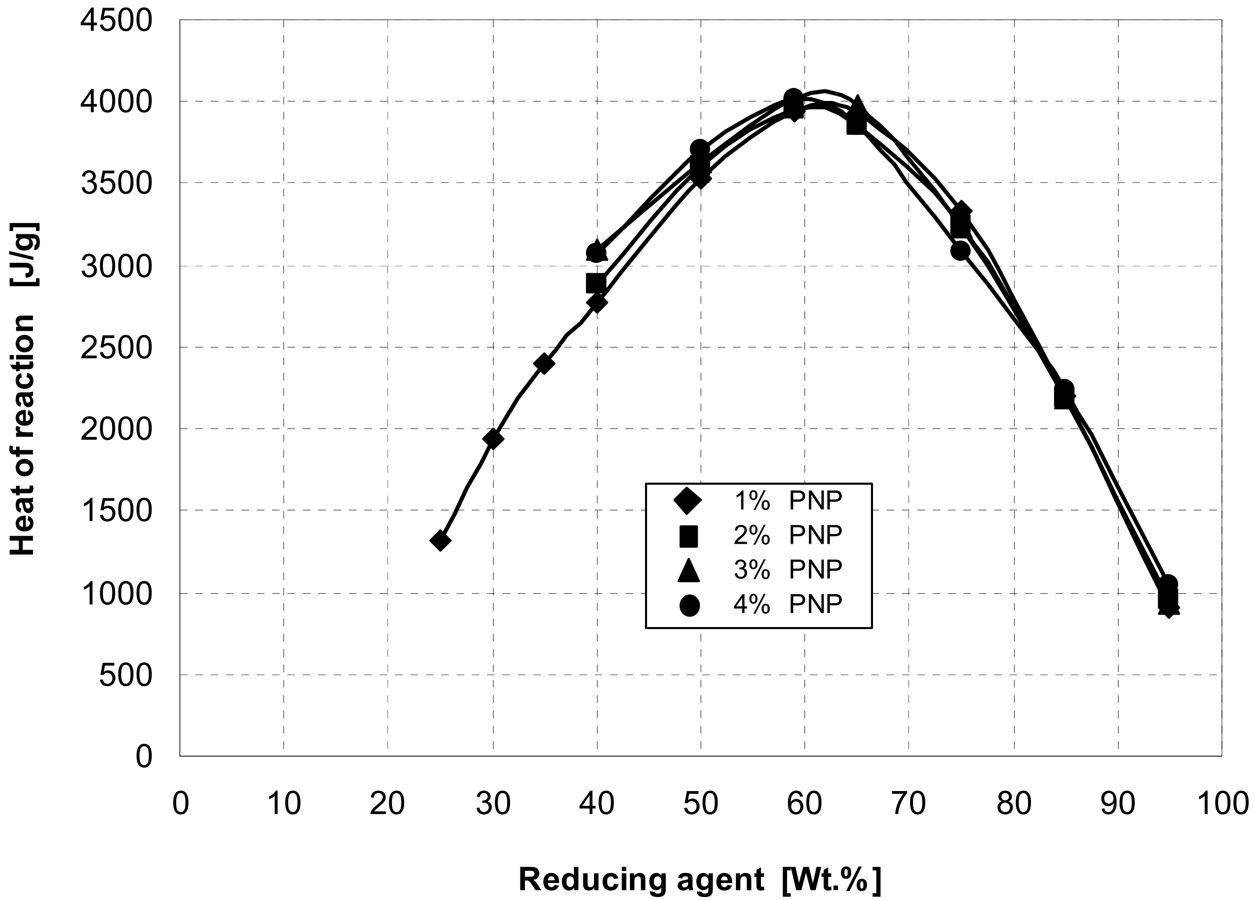


Factors Influencing the Pyrotechnic Reaction

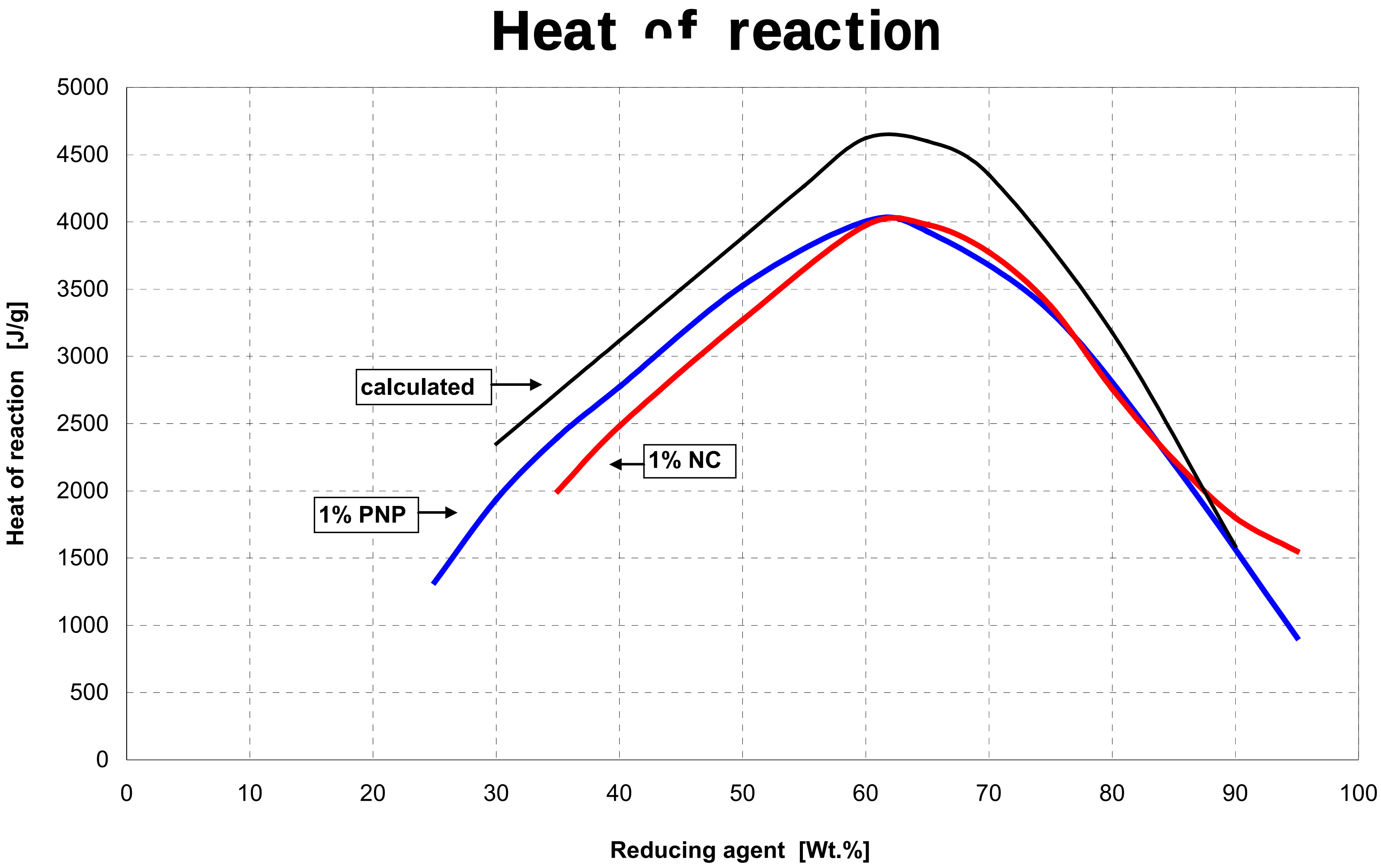
- Type of reducing agent / oxidizer
- Purity / Oxide layer
- Particle size / specific surface
- Oxygen balance
- **Binder type / binder content**
- Mixing procedure

▪ Binder Content

Heat of reaction

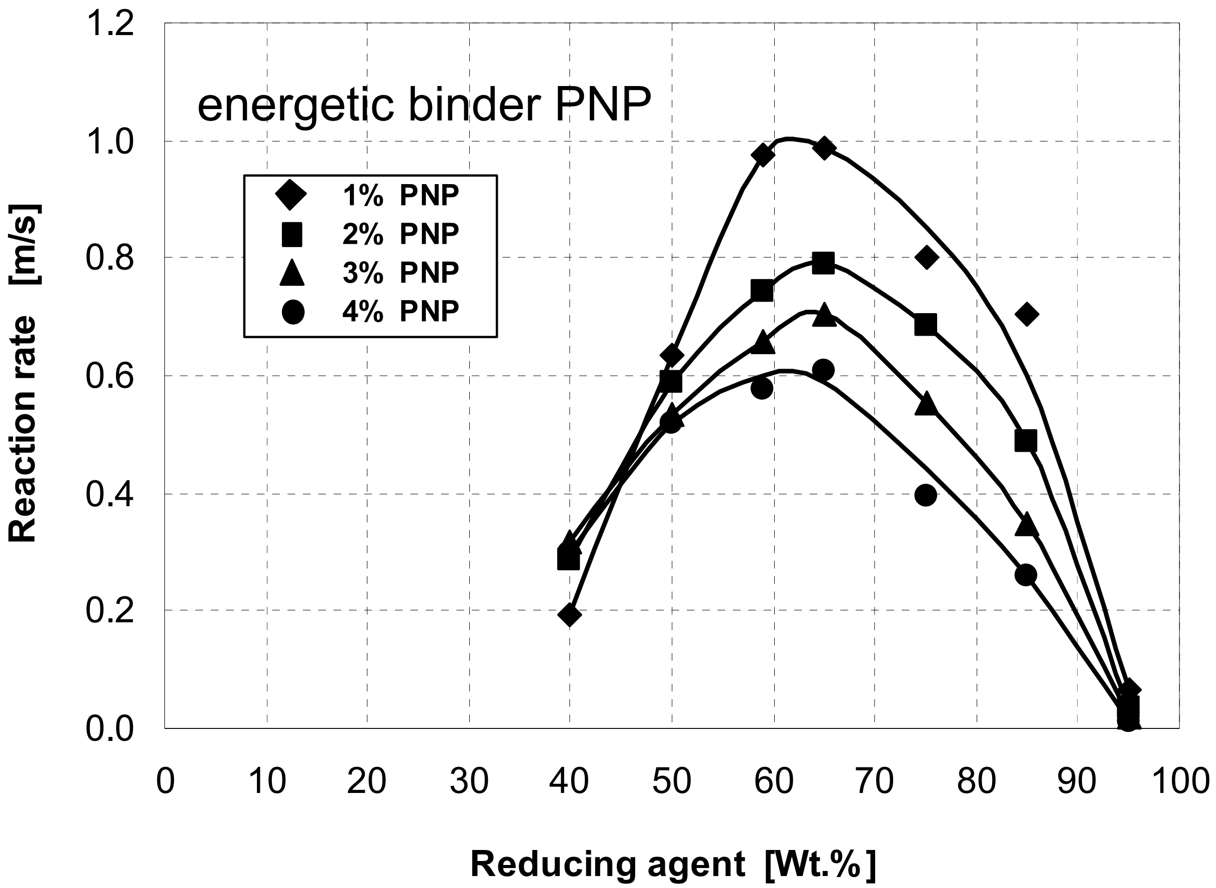


Type of Binder



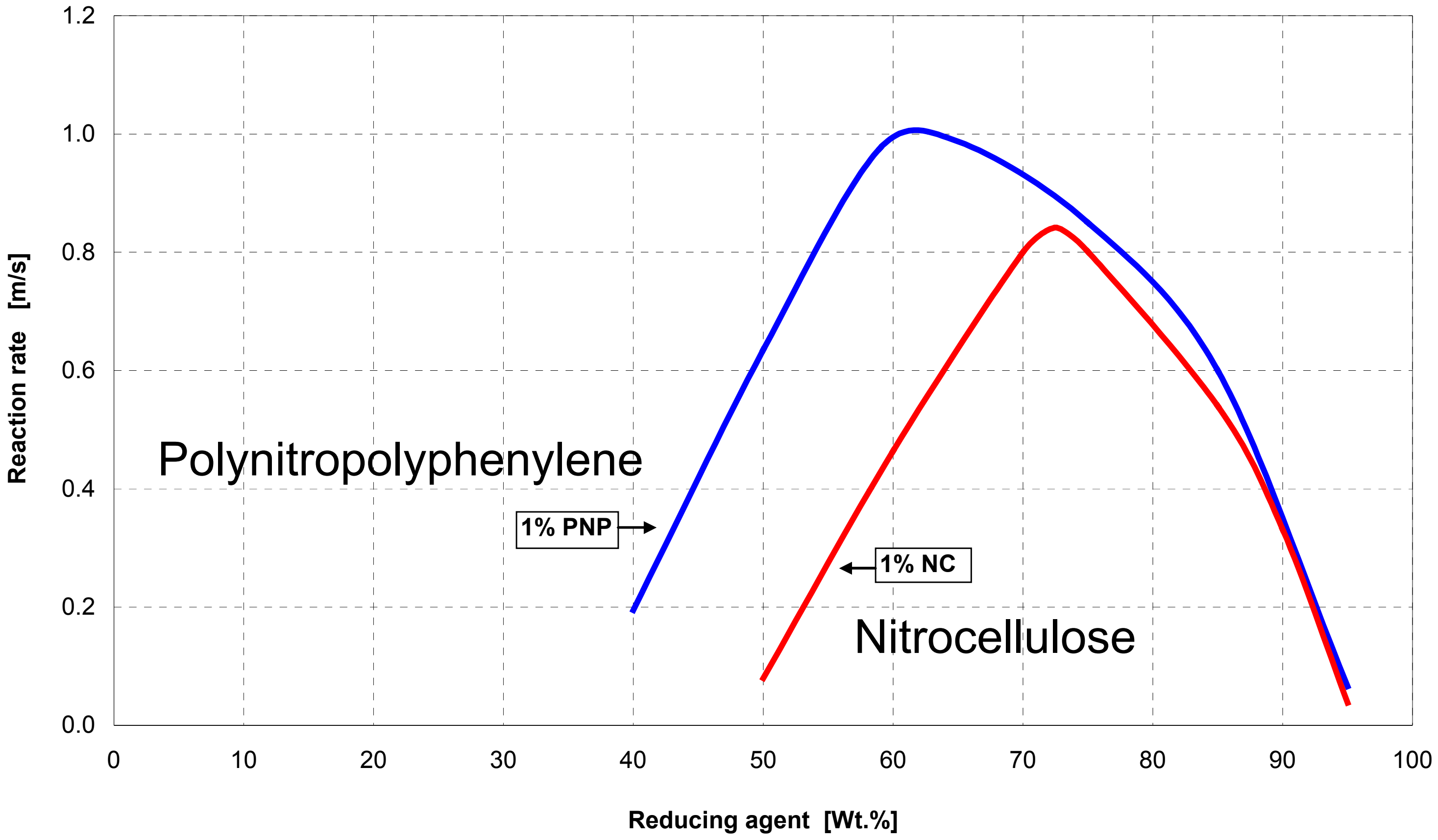
Binder Content

Reaction Rate



Type of Binder

Reaction Rate



Factors Influencing the Pyrotechnic Reaction

- Type of reducing agent / oxidizer
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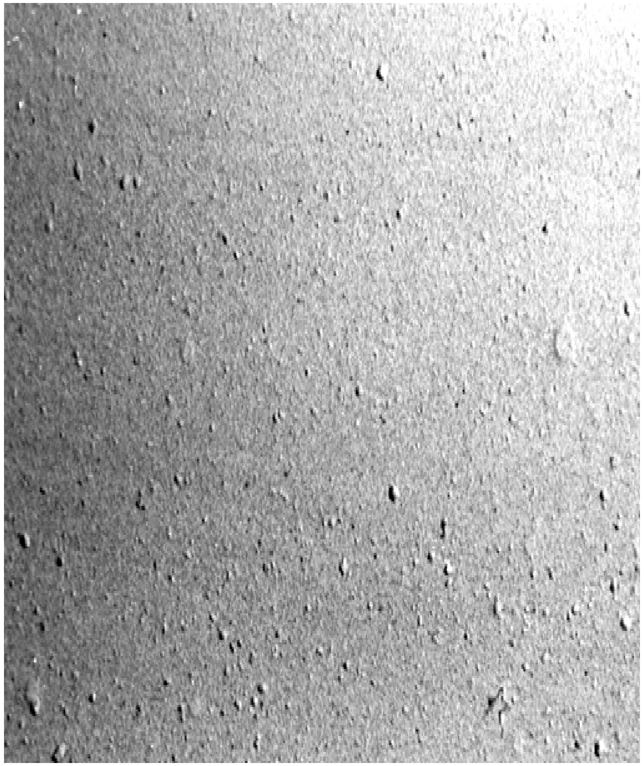
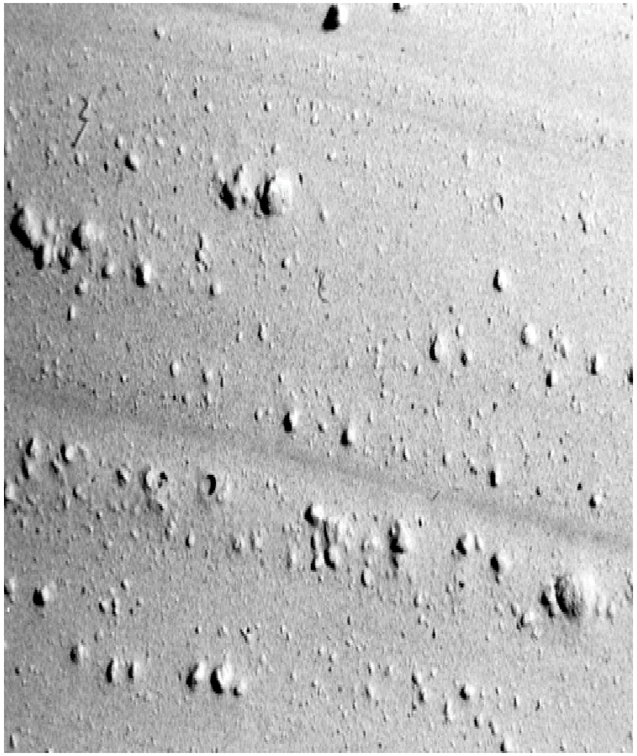
- Mixing procedure

Mixing Process

Ultrasonic Mixing



Turbula Mixing



Summary

- By changing the ingredients, the oxygen balance, the particle size, the type of binder / binder content and the mixing procedure the performance of pyrotechnic compositions can be varied in a wide range
- It is a great advantage to use pyrotechnic compositions consisting of only one oxidizer and one reducing agent
- The oxygen balance influences the thermal behaviour of pyrotechnic compositions

Summary

- The thickness of the oxyd layer on the surface of the reducing agent influences the ignition behaviour

- Inpurities influence the performance of pyrotechnic compositions

▪ Future

- Use of nano particles as reducing agent
- Use of nano structured oxidizers
- Liquid oxidizers incapsulated in nano inclusions of reducing agents

Thank you

for your

attention

Thank you
for your
attention

REASSESSMENT OF THE IDENTITY OF THE BLUE LIGHT EMITTER IN COPPER-CONTAINING PYROTECHNIC FLAMES

Is it really Cu(I)Cl ??

By

Daniel P. Dolata
Pyro Safety
PO Box 160
Amesville, OH

We all *know* the identity of the chemical species that emit colored light in pyrotechnics. Their identities can be found in many books.

species	color
SrCl	deep red
CuO	weak red
SrOH	orange red
CaOH	orange
CaCl	orange
Na	yellow
BaO	dull yellow green
CuOH	pale green
BaCl	deep green
CuCl	deep blue or violet blue
KCl	pale violet
$\mathrm{SrCl} + \mathrm{CuCl}$	purple
$\mathrm{Al2O3}$	black body radiator
MgO	black body radiator
MgCl	transparent

From Introductory Practical Pyrotechnics by Tom Perigrin.

We also know that the blue color from copper flames is only produced in low temperature flames. Two examples:

The blue emission of cuprous chloride can be obtained only in the reducing zone of the flame and at temperatures not in excess of 1000 – 1200° C.

A. Shidlovskiy, Principles of Pyrotechnics, 3^{Rd} Ed, 1964, page 170.

Potassium chlorate would be an ideal choice because of its ability to sustain low reaction temperatures (remember, CuCl is unstable above 1200° C)…

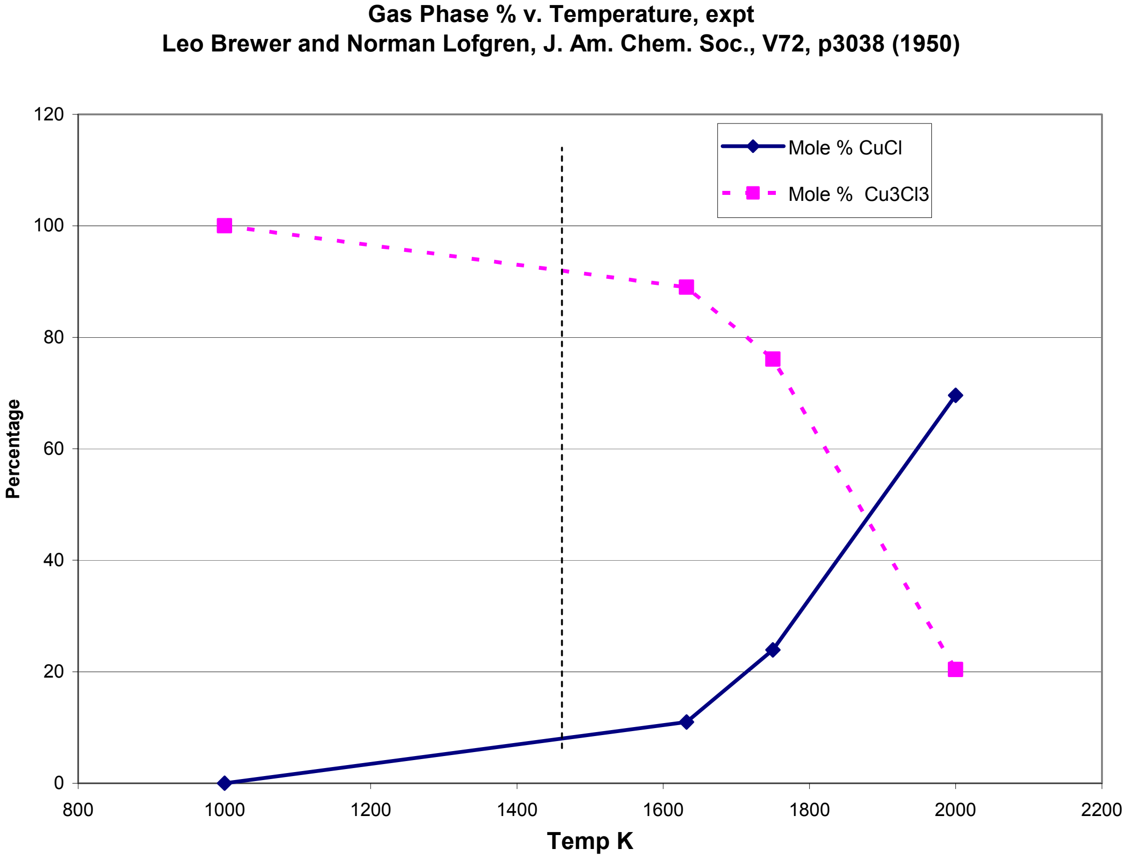
J. A. Conkling, Chemistry of Pyrotechnics, 1985, page 161.

HOWEVER

The assignment of the emitter as CuCl and the requirement for low temperatures due to thermal instability is probably wrong.

Brewer and Lofgren studied the vapor pressure of CuCl gas at several temperatures over molten CuCl in a quartz tube using an argon gas sweep. They also studied the heat of formation of gaseous CuCl by reacting hot HCl vapor with hot solid Cu metal at various elevated temperatures and measuring the vapor pressure.

Brewer and Lofgren, The Thermodynamics of Gaseous Cuprous Chloride, Monomer and Trimer, J. Am. Chem. Soc., V72, p3038 (1950)



In 1972, Guido, Gigli and Spoliti, published a study in which Cu(I)Cl was enclosed in a quartz/stainless steel, or an alumina/molybdenum crucible and heated from 550 to 900 K, and the vapor was effused into and analyzed using a mass spectrometer.

Data for 660 K.

Original Species	Ionized Species	Relative Intensity
Cu_5Cl_5	$Cu_5Cl_5^+$, $Cu_5Cl_4^+$	0.5, 0.25
Cu_4Cl_4	$Cu_4Cl_4^+$, $Cu_4Cl_3^+$	80, 2.5
Cu_3Cl_3	$Cu_3Cl_3^+$, $Cu_3Cl_2^+$	100, 36
$Cu_3Cl_{3(?)}$	Cu_2Cl^+	40
CuCl	CuCl	2

M. Guido, G. Gigli and M. Spoliti, J. Chem. Phys., V57, p3731 (1972)

A. Buchler, J. Stauffer, W. Klemperer, J. Chem. Phys, V40, p3471 (1964)

Microwave examination of the product of chlorine gas on copper metal at 1350 K

Monomer concentration less than limit of detectability

E. Manson, F. De Lucia, W. Gordy, J. Chem. Phys, V62, p1040 (1975)

Similar method to previous paper, but at low pressure 0.01 Torr and at 1000 K.

Monomeric Cu(I)Cl is the predominant species.

A. Potts and M. Lyus, J. Electron. Spectrosc., V13, p305 (1978)

Photoelectron spectroscopy at 1 atm and 1000 K showed a predominance of both the tetramer Cu_4Cl_4 and the trimer Cu_3Cl_3.

Brewer and Lofgren calculated H_f for the monomer and trimer at 1300 K (colligative studies)

Monomer 18.8 ± 4 kcal
Trimer -63.1 ± 2 kcal

Guido, Gigli and Spoliti (mass spectroscopy, 1000 K)

Reaction	ΔH_0 (kcal/mol)
$3\ Cu_3Cl_3 = CuCl + 2\ Cu_4Cl_4$	17.7 ± 0.8
$Cu_4Cl_4 = CuCl + Cu_3Cl_3$	48.4 ± 0.9
$3\ CuCl = Cu_3Cl_3$	-113.5 ± 1.9
$4\ CuCl = Cu_4Cl_4$	-161.3 ± 2.5
$1/2\ (Cu_4Cl_4 = 2\ Cu_2Cl_2)$	37.2 ± 0.5
$2/3\ (Cu_3Cl_3 = Cu_2Cl_2)$	32.2 ± 0.7
$2\ CuCl = Cu_2Cl_2$	-43.6 ± 0.9
$2\ Cu_2Cl_2 = Cu_3Cl_3 + CuCl$	-26.5 ± 0.7

Mao, Liu, Li and Qin used a UV laser to evaporate $CuCl_2$ and then followed the formation of subsequent species using time of flight (TOF) mass spectroscopy. They observed decomposition of $CuCl_2$ to give Cu(I)Cl, followed by collisional congelation to give Cu_3Cl_3 and Cu_4Cl_4.

D. Mao, Z. Liu, R. Li, Q. Qin, Huaxue Wuli Xuebao, V9, p92 (1996)

Van Veen, Baller and De Vries utilized a far UV laser pumping a CuCl target in a TOF mass spectrometer. In this study the predominant species in the gas phase was found to be Cu(I)Cl, with only minor contributions from the dimer and trimer. However, the results are commensurate considering that the temperature of the far UV pulses were calculated to be <u>approximately 6000 K!</u>

NOTE – Cu(I)Cl monomer withstood 6000 K!

G. Van Veen, T. Baller, A. De Vries, J. Appl. Phys., V60, p3746 (1986)

In 1971 M. M. Arski reported a pressure/temperature study that indicated the presence of KCu_2Cl_2 above molten KCl and CuCl

M. Arksi, X. Anorg. Allg. Chem., V386, p345 (1971)

Inspired by this work Bloom and Williams reported the results of a mass spectroscopic analysis of the vapors above a series of binary salt mixtures, including LiCl-CuCl and KCl-CuCl

H Bloom and D. Williams, J. Chem. Phys, V75, p4636 (1981)

MCl-CuCl melt	Relative Intensity M = Li	Relative Intensity M=K
$Cu_3Cl_3^+$	**100**	**100**
M^+	83	2000
$Cu_4Cl_4^+$	15	2
$MCu_2Cl_3^+$	11	2
$MCuCl^+$	**14**	**19**
$M_2CuCl_2^+$	1	0
$CuCl^+$	1	2

Summary of results

Temperature (Kelvins)	Study	MONOMER	TRIMER
660	Mass Spec	2	100 (rel abundance)
1000	Photoelectron	Minor	Predominance
1000	Gas phase pressure	0	100
1000	Mass Spec	2	99
"> 1000"	Laser ablation of $CuCl_2$	Kinetically formed	Thermodynamically preferred
1000K **low pressure**	Cl_2 on Cu	ONLY	0
1350	Cl_2 on Cu	Less than detector limit (1964)	ONLY
1632	Gas phase pressure	11	89
1750	Gas phase pressure	24	76
2000	Gas phase pressure	80	20
6000	UV laser ablation	100	0

Copper Chloride Emissions

	Wavelength, nm	Flame Intensity	Temp of Appearance
System A			1500 K
Green	538.0	4	
	526.2	6	
	515.2	3	
System B			1400 K
Greenish Blue	498.2	2	
	488.5	2	
	488.1	4	
	478.8	2	
System C			1400 K
Greenish Blue	495.0	1	
	494.6	1	
	485.1	1	
	484.7	3	
	475.6	1	
System D			1138 K
Deep Blue	451.6	5	
	443.4	9	
	435.8	1	
	435.4	10	
	428.1	9	
	421.1	3	
System E			1138 K
Deep Blue	449.4	5	
	441.4	1	
	441.2	8	
	433.3	9	
	426.2	1	
	425.9	7	
	418.8	3	
System F			
	417.4 - 369.4	weak	

R Ritschel, Zeit. Phys., V42, p172 (1927)
J. Terrien, Comptes Rendes Acad. Sci. Paris, V201, p1029 (1935)
A. Gaydon, Proc. Royal Soc., V182, p199 (1943)
P. Rao, J. Brody, J. Chem. Phys., V35, p776 (1961)

HOWEVER,

Conkling states:

In an oxygen rich flame, and at temperatures above 1200 C, CuCl is unstable and will react to form CuO and CuOH. CuOH emits in the 525 – 555 nanometer region (green!) and substantial emission may overpower any blue effect that is also present.

J. Conkling, Chemistry of Pyrotechnics, 1985, p 160.

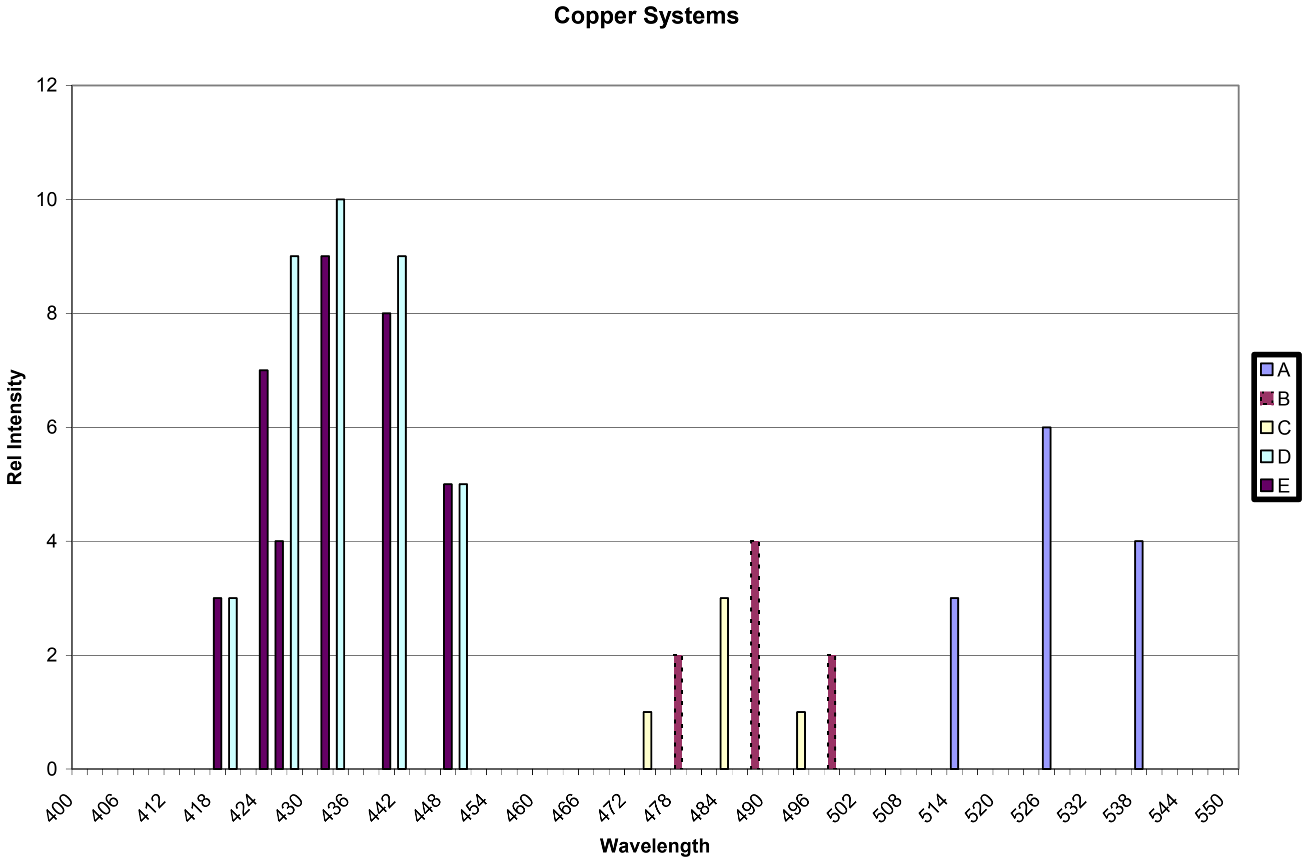
This is the region ascribed to the A system by others. Which is the right assignment?

Perhaps both are right, as Conkling did not specify exactly which peaks to which he was referring.

Wavelength	Species
505.0	Copper hydroxide
515.2	Copper chloride A
524.0	Copper hydroxide
526.2	Copper chloride A
537.0	Copper hydroxide
538.0	Copper chloride A

The copper hydroxide peaks are diffuse, and of lower intensity.
R Mavrodineanu, H Boiteux, Flame Spectroscopy, Wiley and Sons, 1965

Furthermore, the 5 systems described follow Ritz's combination principle and Hartley's law of constant differences, as can be seen when the 5 systems are graphed:



After completing the literature review it was obvious that the phenomenon of emission of blue light from copper-chloride containing flames is much more complex than is commonly thought. To summarize some of the points:

- The flame contains many copper halide species; CuCl, Cu_3Cl_3, Cu_4Cl_4, etc...

- The ratio of these species depends on the temperature

- The flame can also contain other copper species, such as CuO, CuOH, etc...

- The copper chloride spectrum is complex, consisting of several different band systems

- The intensity of those band systems depends on the temperature

Questions

Is the color quality of the blue light affected by:

The formulation (we know the answer is yes, but is it the A,B,C,D,E ratios, or other factors)?

The nature of the copper source?

The amount of the copper source?

The ratio of chlorine to copper?

The flame temperature?

Base mixes were made, and then the variable component was added along with a complimentary amount of K_2CO_3.

The formulation:

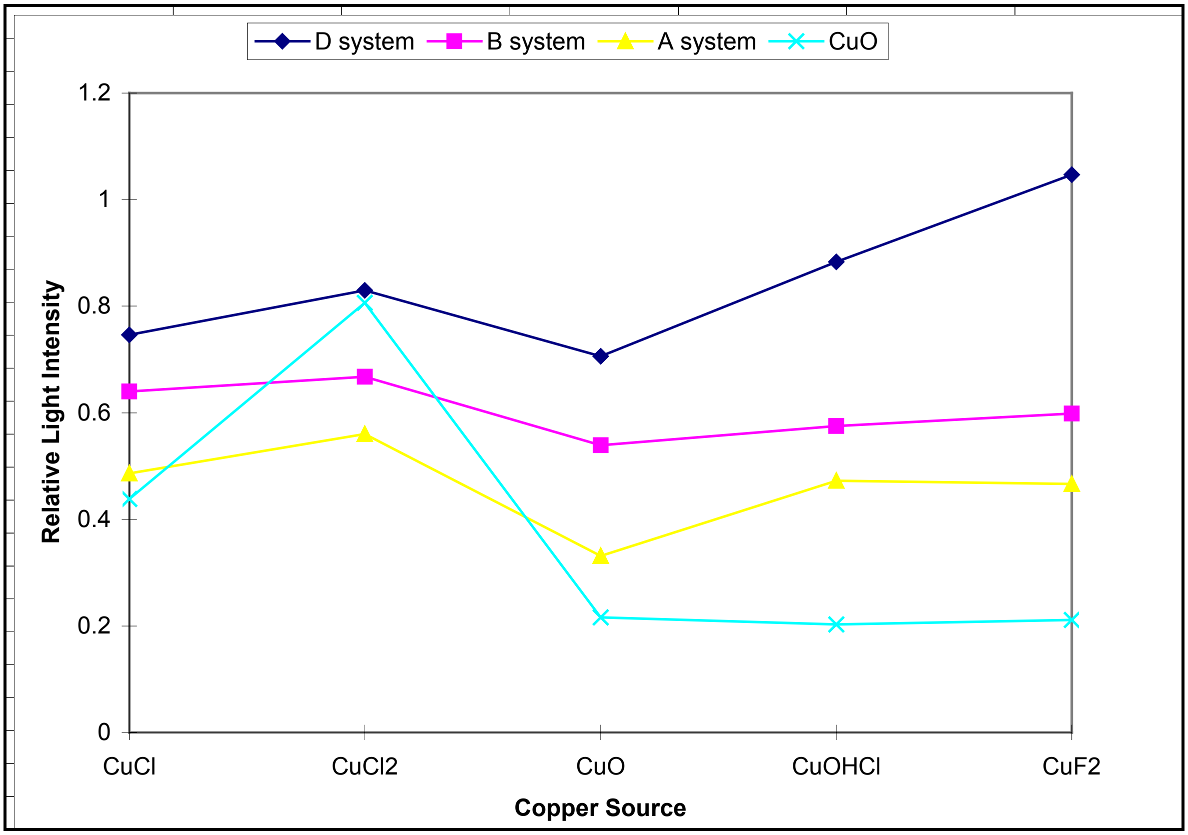
	Shimizu Blue II	modified Blesser #5	Blesser #20
$KClO_4$	66.5		
$KClO_3$		65	
NH_4ClO_4			68
Red Gum	9.9		
Lactose		13	
Hexamine			17
Dextrin	4.8	5	4
CuO	13.4		
CuOHCl		12	11
Parlon	5.4	5	
wt % of Cu	10.7	6.7	6.2
wt % of Cl	20.4 *	25.7 *	23.8
CIE x,y	0.274, 0.356	0.260, 0.329	0.230, 0.234
A : D ratio green : blue	0.70	0.36	0.29
B : D ratio greenishblue : blue	1.14	0.81	.89
C : D ratio greenishblue : blue	0.78	.51	.58

* = not all chlorine from $KClO_x$ will be available to form copper halides

Relative contributions of the D, B, and A systems of copper chloride, and the red system of CuO. The base mix was 67% $KClO_4$, 12% red gum, 3% dextrin, and 8% parlon.

The copper source was 10%.

The spectra were scaled so that the major peak of the CuCl C system had a relative intensity of 1.0



Varying the amount of copper source:

The relative intensities of key peaks from the CuCl A, B and D systems and the red CuO peak as the amount of CuO was varied from 0% to 15%.

The percentages of $KClO_4$, red gum, and parlon were held constant, and a complimentary amount of potassium carbonate was added to so that CuO + K_2CO_3 = 15%

Varying the amount of chlorine donor:

65% $KClO_4$, 10% red gum, and 10% CuO. Parlon was used as a chlorine donor, and the amount was varied from 0% to 10% in 2% steps, and then one sample at 15%. A complimentary amount of K_2CO_3 was added such that parlon + K_2CO_3 = 15%.

It should be remembered that potassium perchlorate can donate some chlorine although it is not normally considered to be an effective chlorine donor. Thus, some peaks from the copper-chloride systems were observed even at 0% parlon. However, there was a substantial contribution from both the red CuO peaks and from the green A system. The domination of the green A system was still present at 2% parlon, but slowly decreased with increasing parlon concentration. The best ratio for the D system was obtained at 8% parlon, and it actually decreased after that point.

Effect of cooling the flame

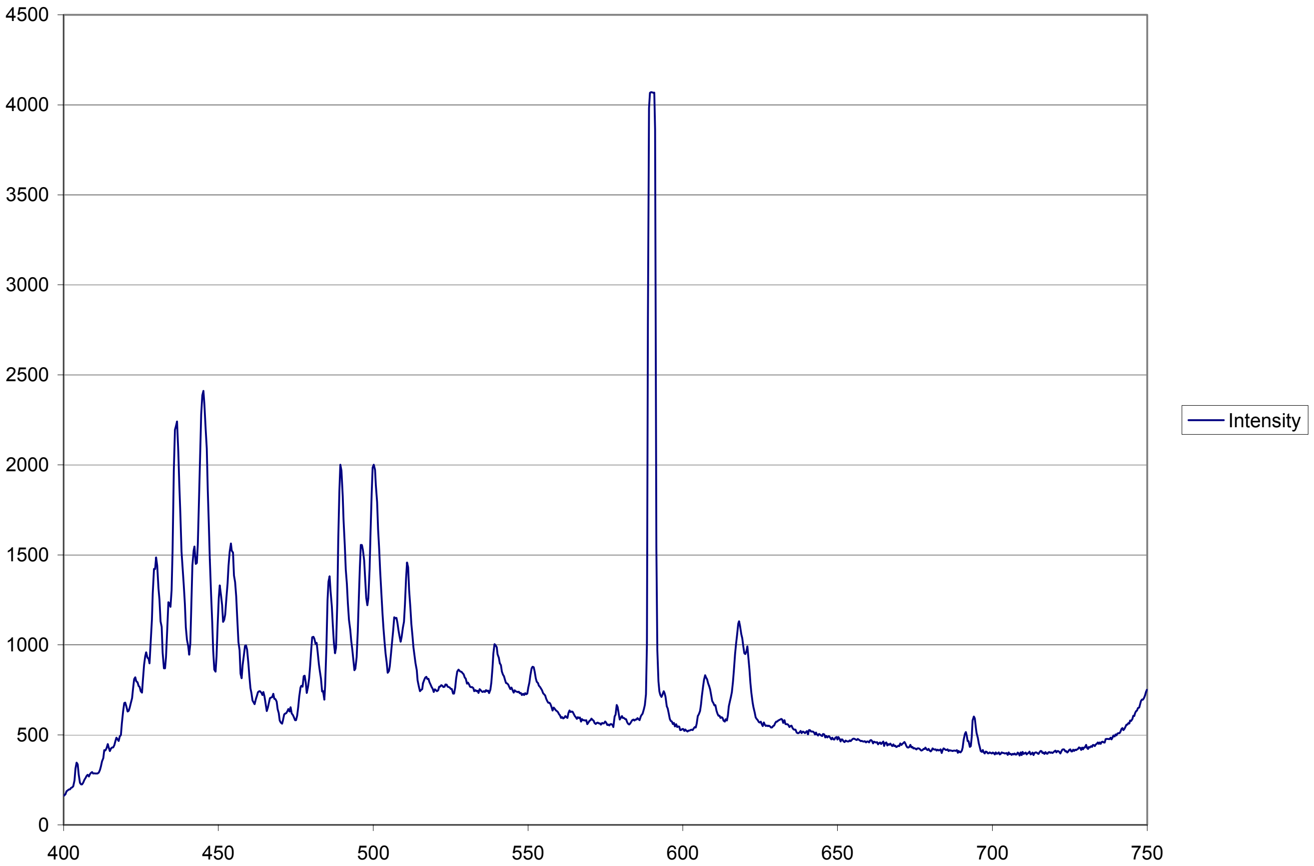
The relative intensities of key peaks from the CuO system, and CuCl A, B and D systems as *additional percentages* of potassium carbonate was added to cool the flame temperature.

25% additional percent of potassium carbonate gave a very small, but intensely blue flame.

A synthesis of the lessons learned:

1) use a low temperature oxidizer such as $KClO_3$
2) use a low temperature fuel that doesn't produce black body radiation
    a. eliminates most organic fuels
    b. eliminates metals
3) make sure the mixture is fuel rich
4) use plenty of chloride donor

65% $KClO_3$
17% S
10% CuCl
5% basic copper carbonate
3% red gum as binder



Some Conclusions

- At “useful” flame temps, copper chloride is the trimer.

- The D and E systems are good for Blue, the B and C systems are mediochre, and the A system is green!

- One can vary the ratios of D&E to B&C to A. Precise control is still elusive.

- The ratio of D&E to B&C and to A is fixed at very low copper concentrations. However, increased concentrations of copper serves to improve the ratio of blue light to black body radiation and/or other color contaminations.

- Increasing the amount of chlorine is desirable up to a medium percentage, after which it is detrimental. The optimum percentage probably varies for each class of compositions.

- Reducing the flame temperature does improve color quality, although the old explanation of “destruction of the Cu(I)Cl molecule” does not seem to be correct.

Based on this, Brewer and Lofgren calculated H_f for the monomer and trimer at 1300 K

Monomer	18.8 ± 4 kcal
Trimer	-63.1 ± 2 kcal

Semi empirical calculations using Spartan 5.0.2 running on an SGI Octane running IRIX 6.5 were performed. The basis set was PM3(transition), and a full geometry optimization was run. Keywords included NOSYMTRY to suppress symmetry based artifacts. Temperature correction was not performed.

Monomer	30.82 kcal
Trimer	-67.43 kcal

IGNITION OF ALUMINUM POWDERS UNDER DIFFERENT EXPERIMENTAL CONDITIONS

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Defense Threat Reduction Agency (K. Kim, W. Wilson)
Office of Naval Research (J. Goldwasser)
Department of Navy, Crane Division, (R. Shortridge)

July 10, 2004

The 1st Workshop on Pyrotechnic Combustion Mechanisms

Fort Collins, CO

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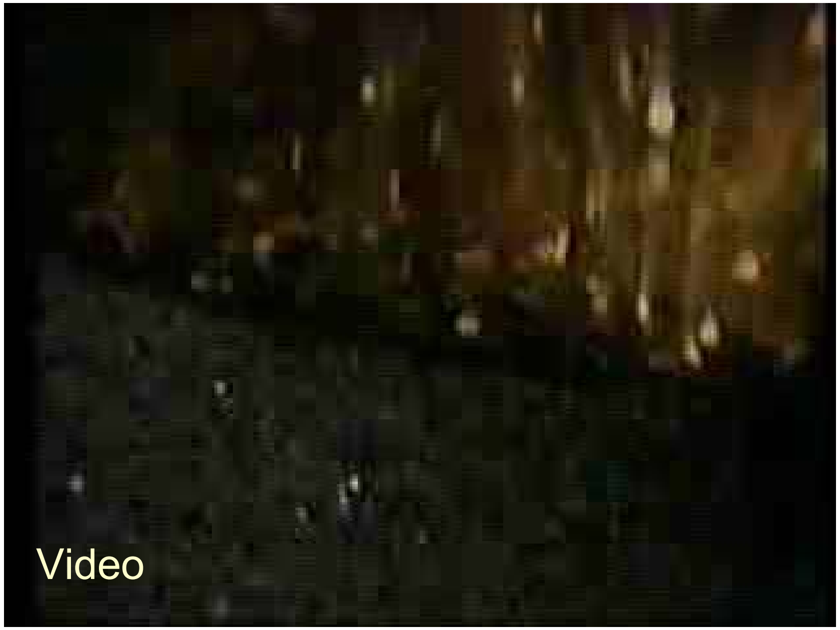
Aluminum powders in energetic materials

- Aluminum is an attractive solid fuel
  - High combustion enthalpy
  - High flame temperature
  - Low cost
  - Non-toxic products
- Combustion rates need to be increased for a number of applications
- Long ignition delays and high ignition temperatures restrict applications
- Studies of aluminum ignition and combustion active during five decades
- Most work deals with combustion; ignition processes are less understood in general

Combustion of aluminized solid propellant

United Technologies, Pratt & Whitney
Chemical Systems Division

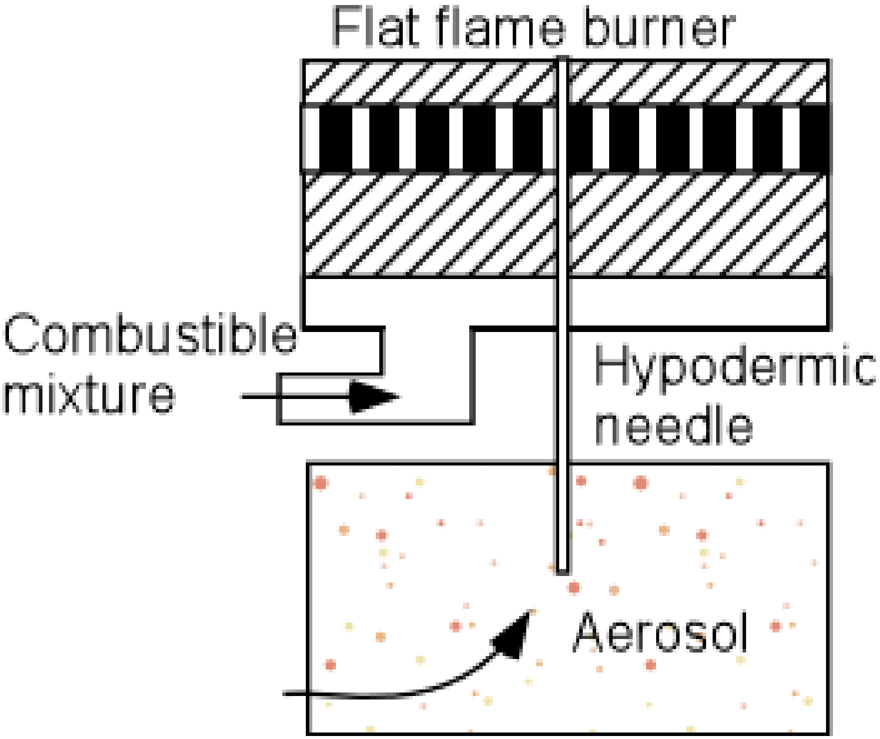
19% Al, HTPB/AP (Tactical Booster)
100 PSI



www.csar.uiuc.edu/~tlj/aluminum.htm

Ignition of aluminum: experimental results for powders

Streaks above the burner show ignition



- Individual aluminum particles entrained in combustion gases
- Spherical aluminum powder, 15 – 67 µm diameter
- Gases used: propane, oxygen, and nitrogen
- Ignition occurs when gas temperature exceeds **1940 ºC**

R. Friedman, A. Macek, *Combust. Flame*, 6, 1962, pp. 9-19

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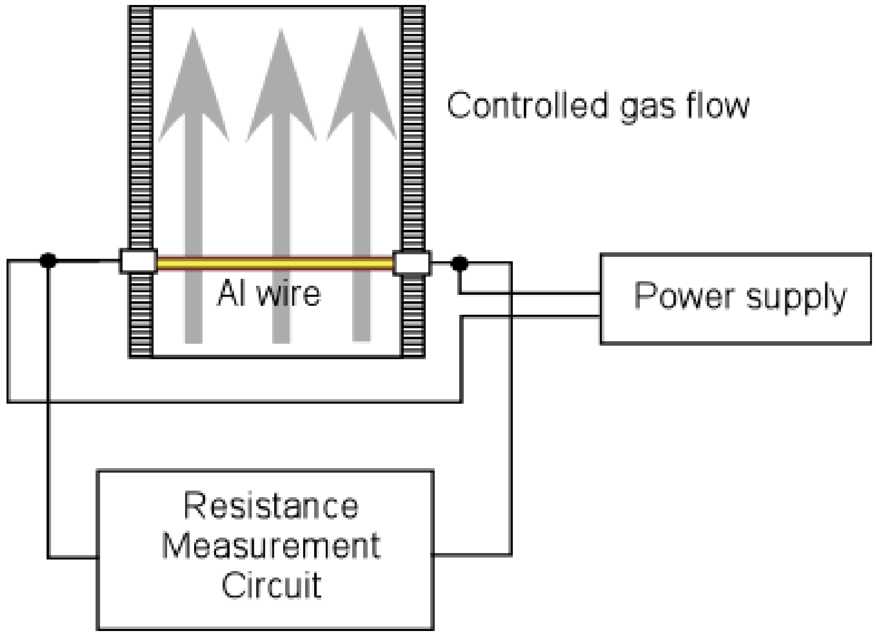
Ignition of aluminum wires

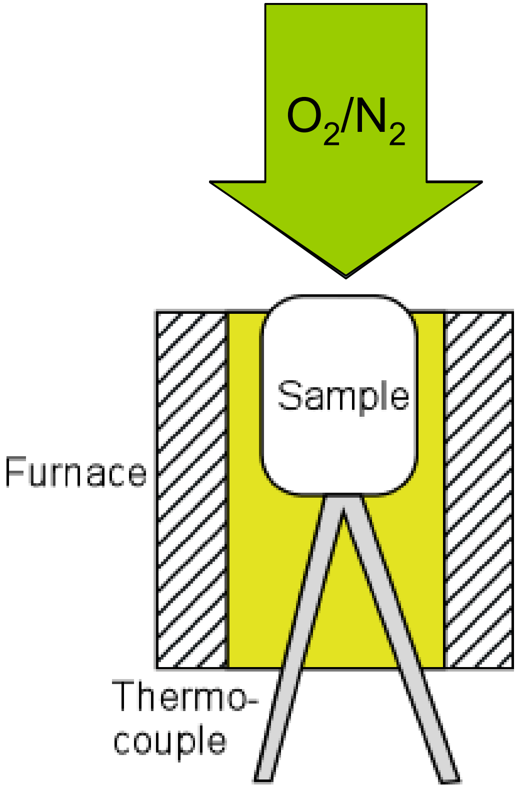


- A laminar gas flow produced in a rectangular tube
- Wire is heated electrically in controlled environment
  - Oxygen
  - Carbon dioxide
- Heating is conducted with
  - constant power
  - stepwise power increase
  - exponentially increasing power
- For 30 - 50 µm diameter wires ignition in pure oxygen occurred at **1640 – 2000 ºC**.

Early work by Brzustowski and Glassman, 1967, Kuehl, 1965

A.G. Merzhanov, Y.M. Grigorjev, Y.A. Gal'chenko, *Combust. Flame* 29 1977, pp. 1-14

Ignition of aluminum cylinders (10 mm diam, 10 mm height)



- **Experiments with natural oxide removed**:
    - Aluminum sample pre-heated in argon
    - After pre-heat, argon is replaced with the oxidizing mixture
- Critical ignition temperatures increase from **1650 to 1950 ºC** as ambient pressure increases from 10 to 100 kPa

- **Experiments with natural oxide**
    - Heating in O_2/N_2 mixture
    - Experiments at 8 and 41 kPa
- Ignition temperatures decrease from **2050 ºC to 1650 ºC** when heating rates increase from 2 to 9 ºC/s.

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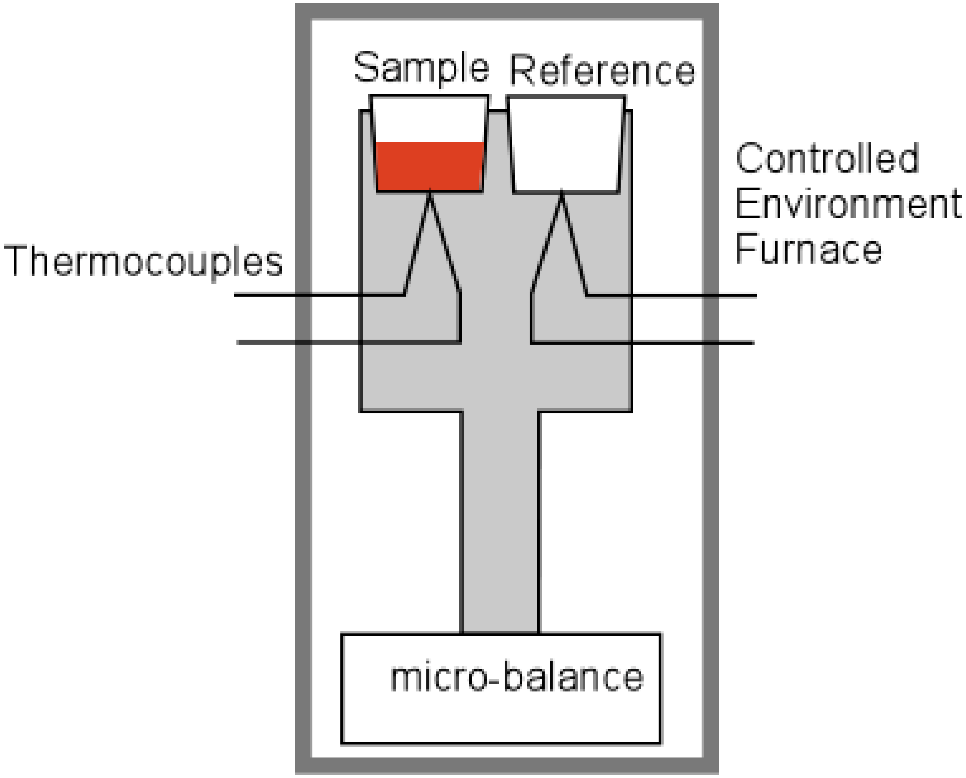
S.Yuasa, Y. Zhu and S. Sogo, *Combust. Flame*, 108,1997, pp. 387-390

Ignition of aluminum nano-powders and flakes

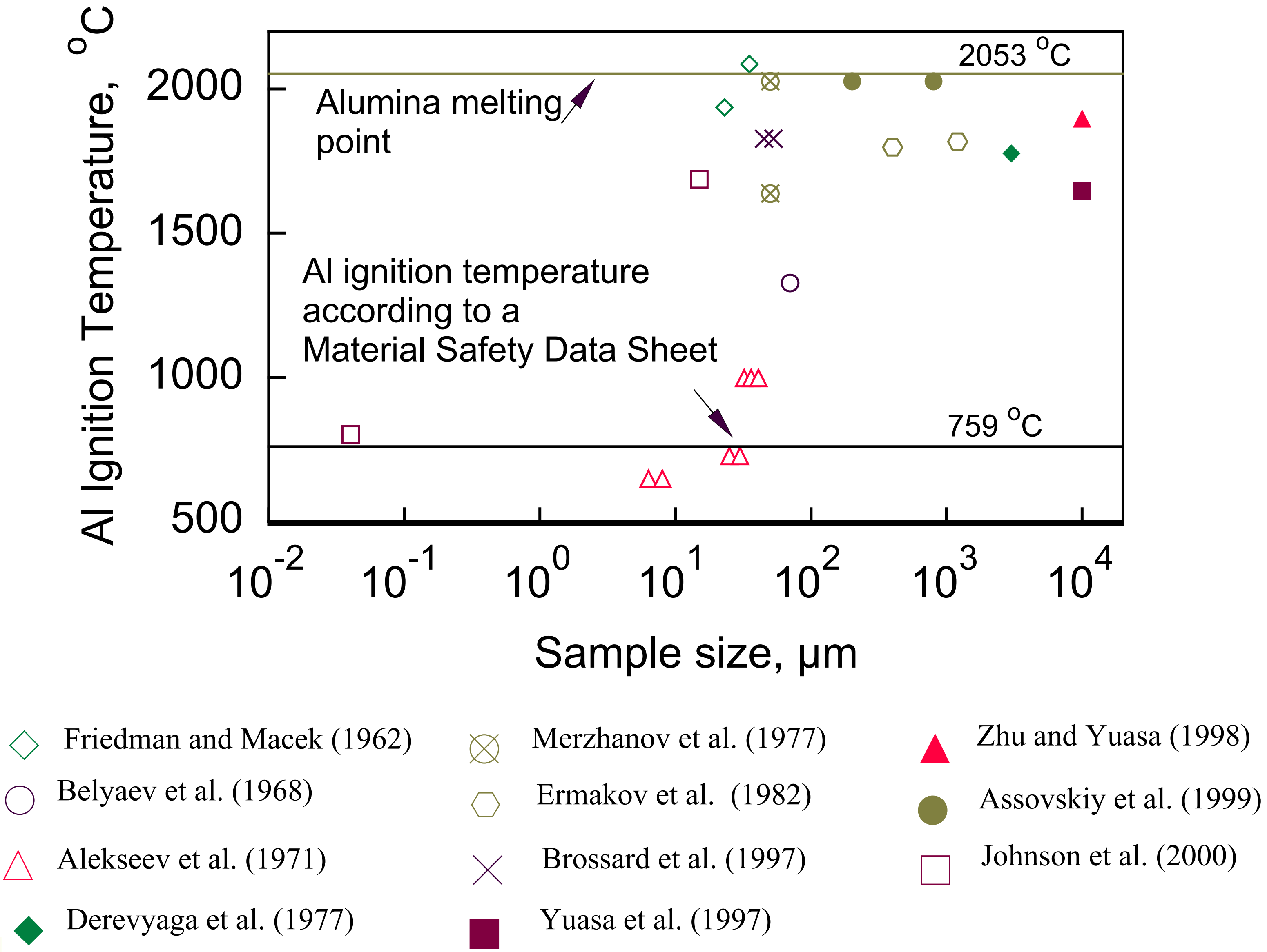


- Particles and flakes ignited upon their heating in oxygen in thermal analyzer
- Ignition is detected by strong heat effect and rapid mass increase
- Aluminum nanopowders and flakes ignite between **570 and 800 ºC**

C. Johnson, T. Parr, D. Hanson-Parr, R. Hollins, S. Fallis, K. Higa, *Proc. 37-th JANNAF Combust. Subcomm. Meeting,* November 2000, pp. 539-551

E.L. Dreizin, M. Schoenitz, M. Trunov, (2004) submitted to *Comb. Flame*

Summary of experimental data on aluminum ignition temperature

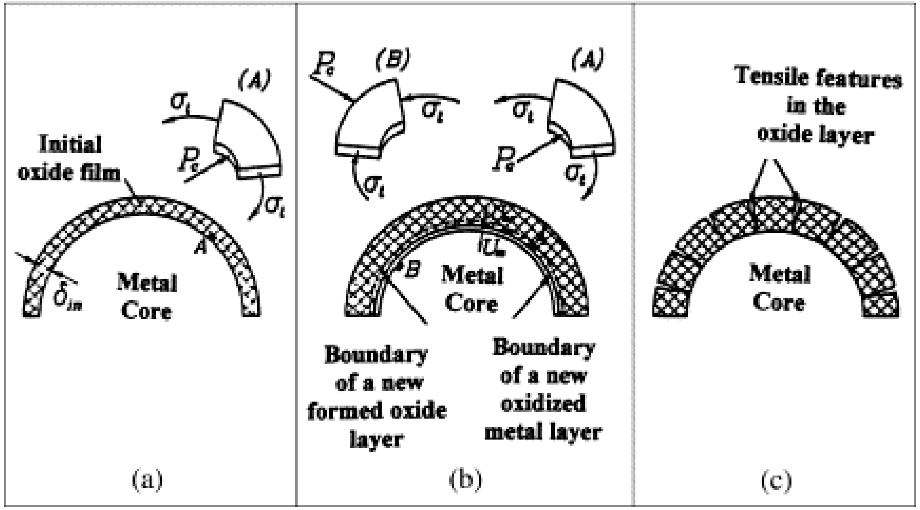


Models of aluminum ignition: Fixed Ignition Temperature

- **Oxide coating melts; bare aluminum surface exposed and ignited**
  - R. Friedman, A. Macek, *Combust. Flame*, 6, 1962, pp. 9-19
  - D.K. Kuehl, *AIAA Journal* 3(12) 1965, p. 2239
  - K. P. Brooks, M.W. Beckstead, *J of Prop. Power* 11, 1995, pp. 769-780
- Ignition temperature is fixed at 2053 ºC, or arbitrarily between 1700 and 2100 ºC.
- This approach is adequate for many experiments in which larger aluminum particles are used
- It is inadequate for finer aluminum particles which are likely to be used in many practical combustion systems

Models of aluminum ignition: Stress in Oxide Scale

- **Oxide coating breaks up due to mounting mechanical stresses and bare aluminum surface ignites**
  - V. Rosenband and N. Vaganova *Combust. Flame* 88, 1992, pp. 113-118
  - V. Rosenband *Combust. Flame*, 137, 2004, pp. 366-375
  - S. Yuasa, Y. Zhu, S. Sogo, *Combust. Flame* 108, 1997, pp. 387-396
- Ignition temperature is poorly defined because of insufficient data on mechanical properties of oxide films at elevated temperatures



- Ignition is unlikely to be predicted at the temperatures exceeding ½ T_{Al2O3} melting, e.g., above 1000 ºC, when deformations of oxide are plastic
- Difficult to explain experimental results with high ignition temperatures
- Ignition is predicted to occur at temperatures exceeding the aluminum melting point (660 ºC)
- No explanation for ignition of nanopowders and flakes below the aluminum melting point

Models of aluminum ignition: Exothermic Oxidation

- **Oxide scale grows in oxidizing environment and the heat release due to oxidation is compared to external particle heating or heat losses. Ignition is predicted by a heat transfer model**
  - A.V. Fedorov, Y.V. Kharlamova *Comb. Expl. Shock Waves* 39, 2003, pp 544-547
  - A.G. Merzhanov, Y.M. Griogorjev, Y.A. Galchenko, *Combust. Flame* 29, 1977, pp 1-14
  - H. Rode, V. Hlavacek, H. J. Viljoen, J.E. Gatica, *Comb. Sci. and Tech*. 88, 1992, pp. 153-175
  - P. George, P.E. DesJardin, *ASME Proceedings* HT2003-47499, 2003
- Typical expression for the oxide growth rate is

$$\frac{dh}{dt} = K\frac{C_{oxidizer}}{h}\exp\left(-\frac{E}{RT}\right)$$

- Activation energy *E* and pre-exponent, *K*, are selected to describe the experiment

Exothermic oxidation models: parameters selection

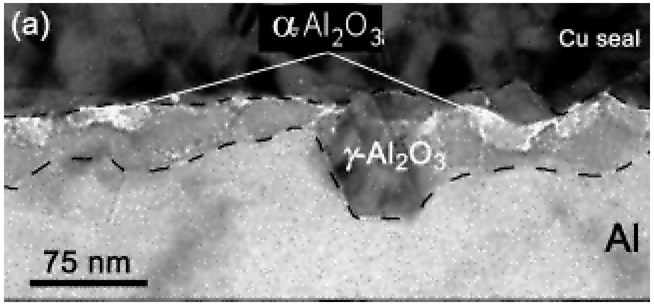
- Activation energies **used** by different researchers **to describe** oxidation:
  - 71 kJ/mol (Merzhanov et al., 1977, Fedorov, Kharlamova, 2003)
  - 83.8 kJ/mol (Gurevich et al., 1970)
  - 95.5 kJ/mol (George, DesJardin, 2003, Tao, 2002, Roberts et al., 1993)
  - 149.6 kJ/mol (Alekseeva, Gyrevich, Ozerov, 1967)

- Activation energies for heterogeneous aluminum oxidation **reported** by different researchers
  - 77.9 kJ/mol (Kiselev, Leipinskikh,1974)
  - 146 kJ/mol (Elytin, Mitin, Samotekin, 1971)
  - 394 kJ/mol (Tompa, Boswell, Skahan, Gotzmer, 1997)
  - 418 kJ/mol (Mitin, Samoteikin, 1971)
  - **No single value possible to assign** (Bergsmark, Simensen, Kofstad, 1989)

How to model oxidation of aluminum powders?

- Growth of oxide film is a complex process
  - Many alumina polymorphs exist
  - Different polymorphs grow at different rates
  - Different polymorphs have different properties
- Mechanistic understanding of processes occurring during thermal oxidation of aluminum and causing oxide evolution is needed to understand and model ignition

Bright field electron micrographs of a cross-section of an initially bare Al(4 3 1) substrate oxidized at 500 ºC



L.P.H.Jeurgens, W.G. Sloof, F.D., Tichelaar, E.J. Mittemeijer, *Thin Solid Films* 418, 2002, pp. 89-101

What do we know about properties and phases of aluminum oxide?

- Common route of phase transformations in alumina film:
  - **Amorphous film ? γ ? δ ? θ ? α-Al_2O_3**

This transition could expose Al surface!

- Alumina phase densities, g/cm^3

– Amorphous film	3 - 3.1
– γ, δ, θ	3.6 – 3.67
– α-Al_2O_3	3.99

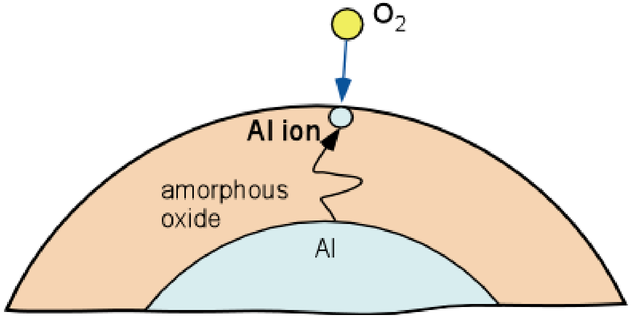
- Amorphous film is stabilized when its thickness is less than **critical** (0.5 – 5 nm)
- Nano-crystalline transition alumina phases (e.g., γ-Al_2O_3) are energetically and thermodynamically **stable** at large specific surface areas
- Grain size of α-Al_2O_3 is at least an order of magnitude greater than that of the parent transition alumina, a transition occurs rapidly once a "**critical**" size nucleus is formed

I. Levin, D. Brandon *J. Am. Ceram. Soc.*, 81, 1998, pp. 1995-2012

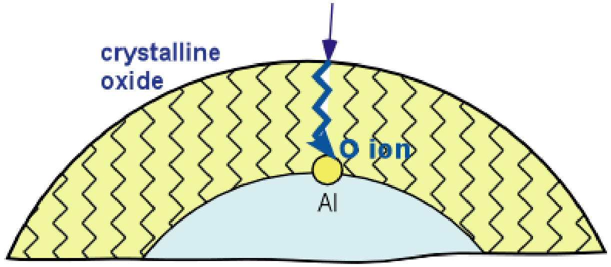
J.M. McHale, A. Auroux, A.J. Perotta, A. Navrotsky, *Science* 277, 1977, pp. 788-791

L.P.H.Jeurgens, W.G. Sloof, F.D., Tichelaar, E.J. Mittemeijer, *Thin Solid Films* 418, 2002, pp. 89-101

Oxidation rate limiting processes



- Amorphous alumina:
  - Outward diffusion of aluminum cations



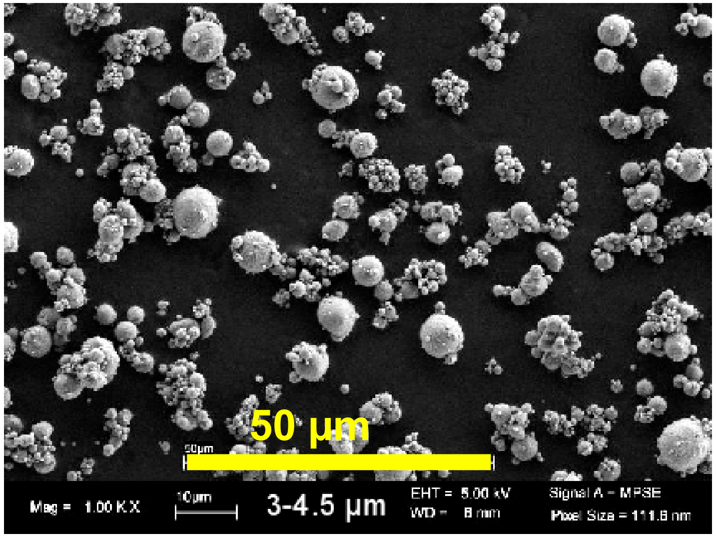
- Crystalline alumina phases:
  - Inward diffusion of oxygen anions
  - in polycrystalline films the **grain boundary** diffusion is the rate-limiting process

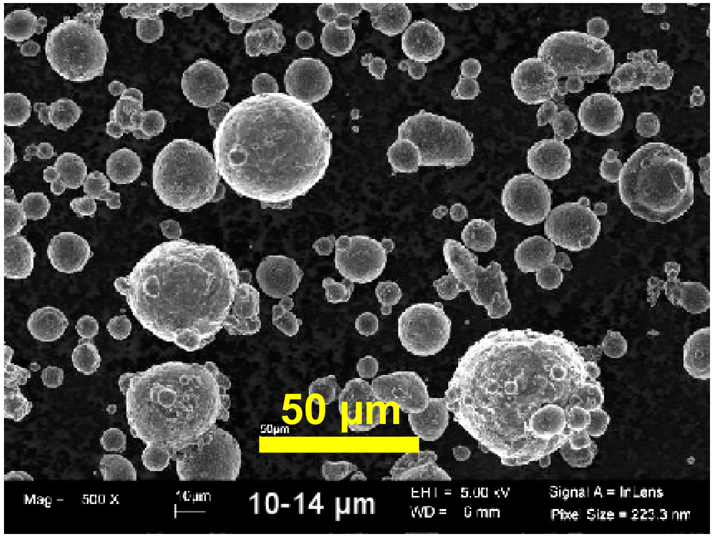
L.P.H. Jeurgens, W.G. Sloof, F.D. Tichelaar, E.J. Mittemeijer, *J. Appl. Phys*. 92, 2002, pp 1649-1656
O.A. Riano, J. Wadsworth, O.D. Sherby, *Acta Materialia* 51, 2003, pp. 3617-3634

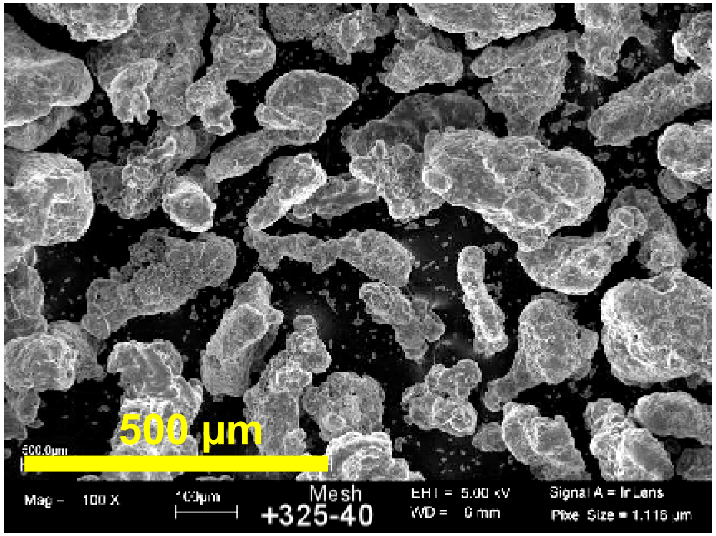
Objectives of this research

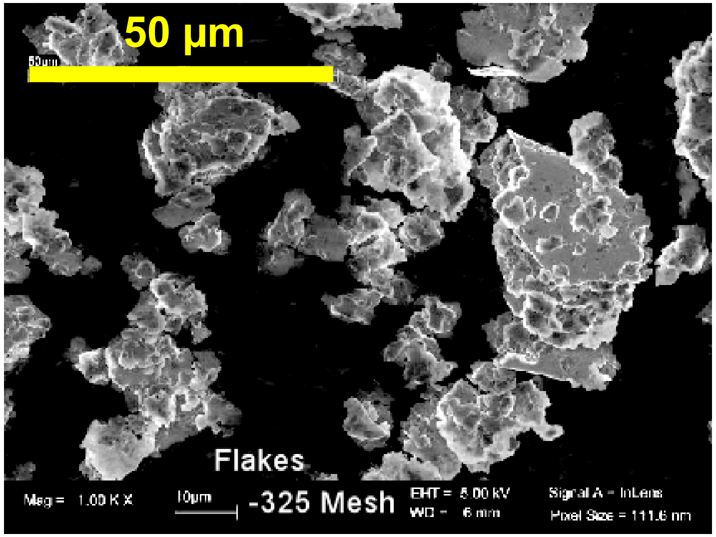
- Identify the processes occurring during oxidation of aluminum powders
- Determine whether transitions between different alumina polymorphs occur
- Determine whether the occurring transitions affect the oxidation kinetics
- Develop a mechanistic model of aluminum ignition taking into account processes of its oxidation

Materials


50 µm
50µm
Mag = 1.00 K X
10µm
3-4.5 µm
EHT = 5.00 kV
WD = 6 mm
Signal A = MPSE
Pixel Size = 111.6 nm


50 µm
50µm
Mag = 500 X
10µm
10-14 µm
EHT = 5.00 kV
WD = 6 mm
Signal A = InLens
Pixel Size = 223.3 nm


500 µm
500.0µm
Mag = 100 X
100µm
Mesh
+325-40
EHT = 5.00 kV
WD = 6 mm
Signal A = InLens
Pixel Size = 1.116 µm


50 µm
50µm
Flakes
Mag = 1.00 K X
10µm
-325 Mesh
EHT = 5.00 kV
WD = 6 mm
Signal A = InLens
Pixel Size = 111.6 nm

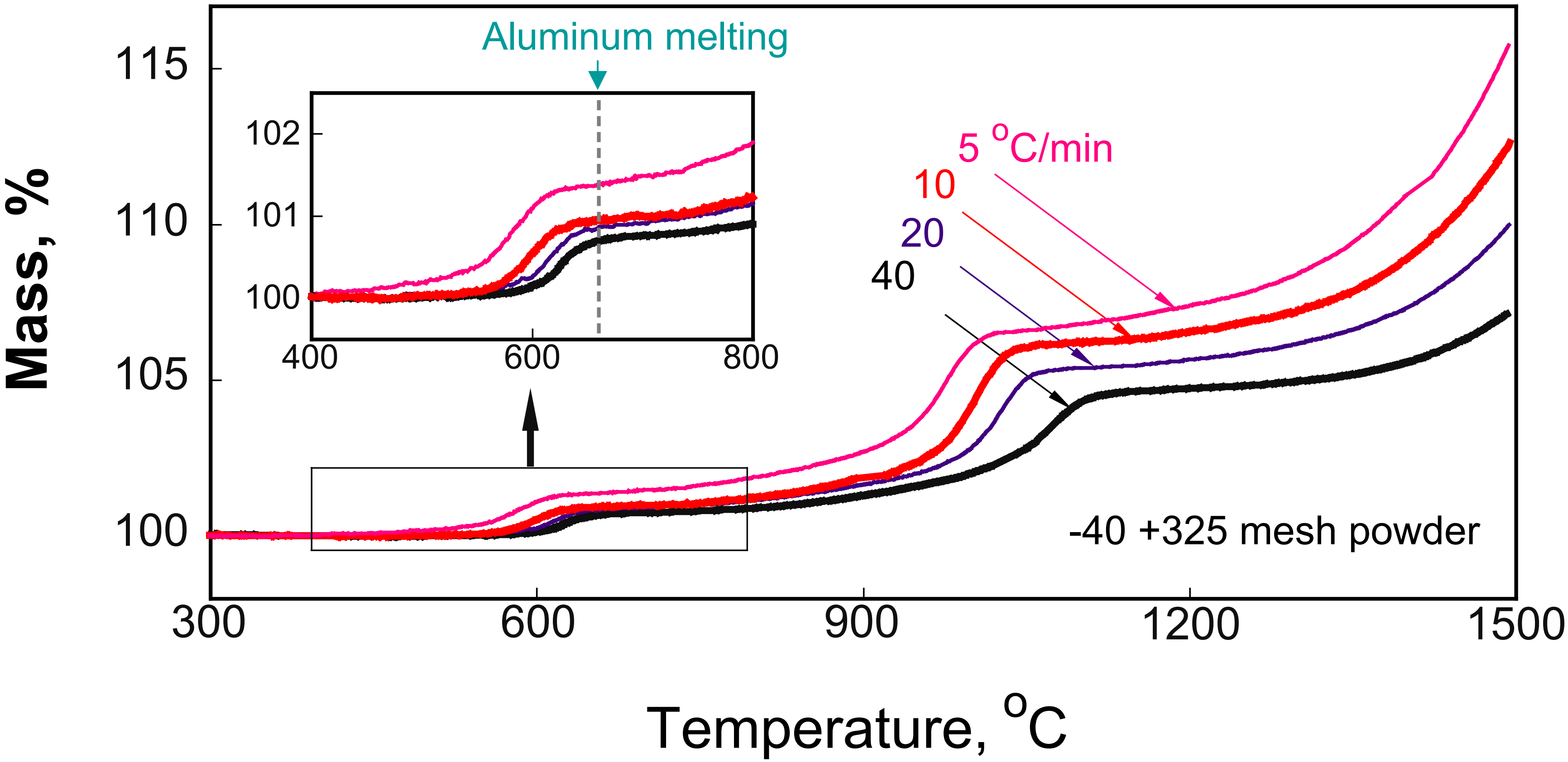
Particle size characterization

Powder ID	Specific surface, S_{BET}, m^2/g	BET diameter, d_{BET}, µm	Laser Light Scattering: Area mean diameter, µm
Spheres 3 - 4.5 µm	1.15	1.93	3.9
Spheres 10-14 µm	0.41	5.42	16.4
-40+325 Mesh	N/A	N/A	201.1
Flakes -325 Mesh	7.41	N/A	N/A

Experimental

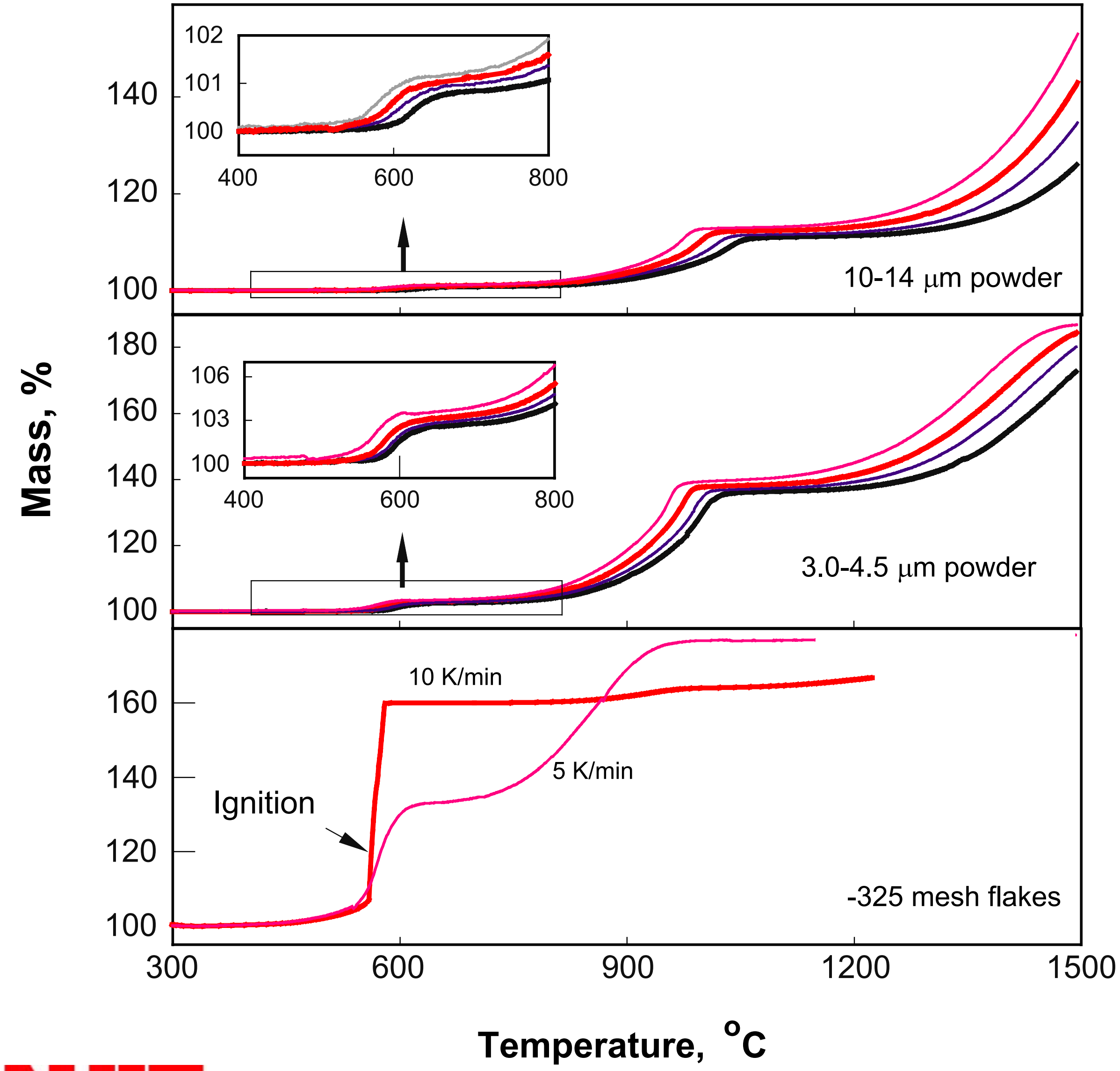
- TGA/DTA: Netzsch Simultaneous Thermal Analyzer STA409
- Alumina sample holders
- Temperature range: 20 – 1490 ºC
- Environment: 80% oxygen 20 % argon
- Heating rate varied from 5 to 40 ºC/min
- Samples quenched at specified temperatures
- Formed oxide scales investigated using XRD/SEM

TGA Results



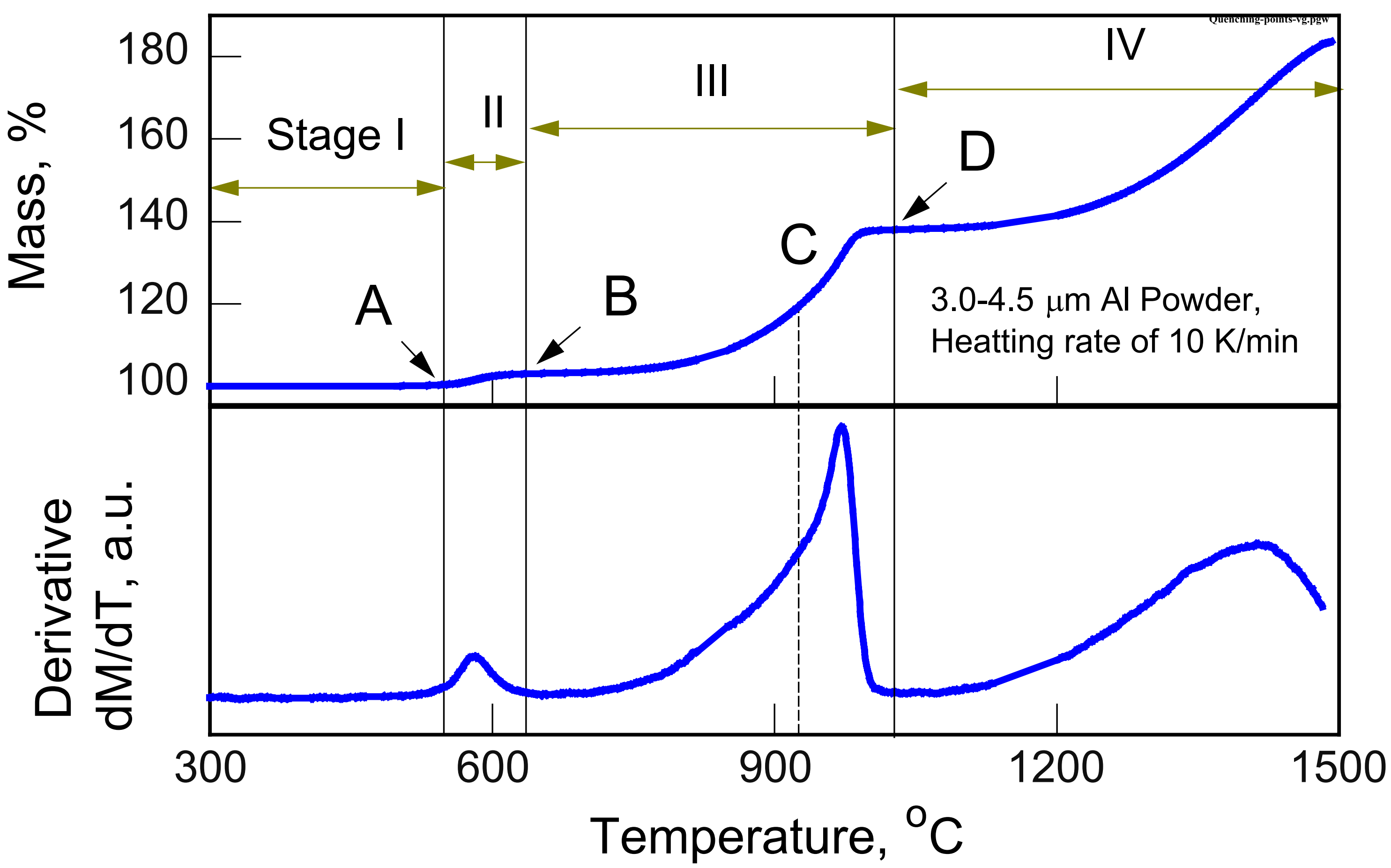
- Oxidation occurs in steps
- The first step occurs at 600 ºC, before melting
- No increase in the oxidation rate is observed during aluminum melting

Summary of TGA measurements for different powders



- Stepwise oxidation is well reproducible
- Flakes with high specific surface (approaching this of nanopowders) ignite during the first oxidation step at higher heating rates
- Nanopowders (Alex) oxidize similar to flakes, ignition is also observed under 600 ºC

Stages in oxidation of aluminum powders



- Characteristic temperatures identified to obtain the **partially oxidized samples**
- Analysis of the produced oxide polymorphs needed to determine processes governing different oxidation stages

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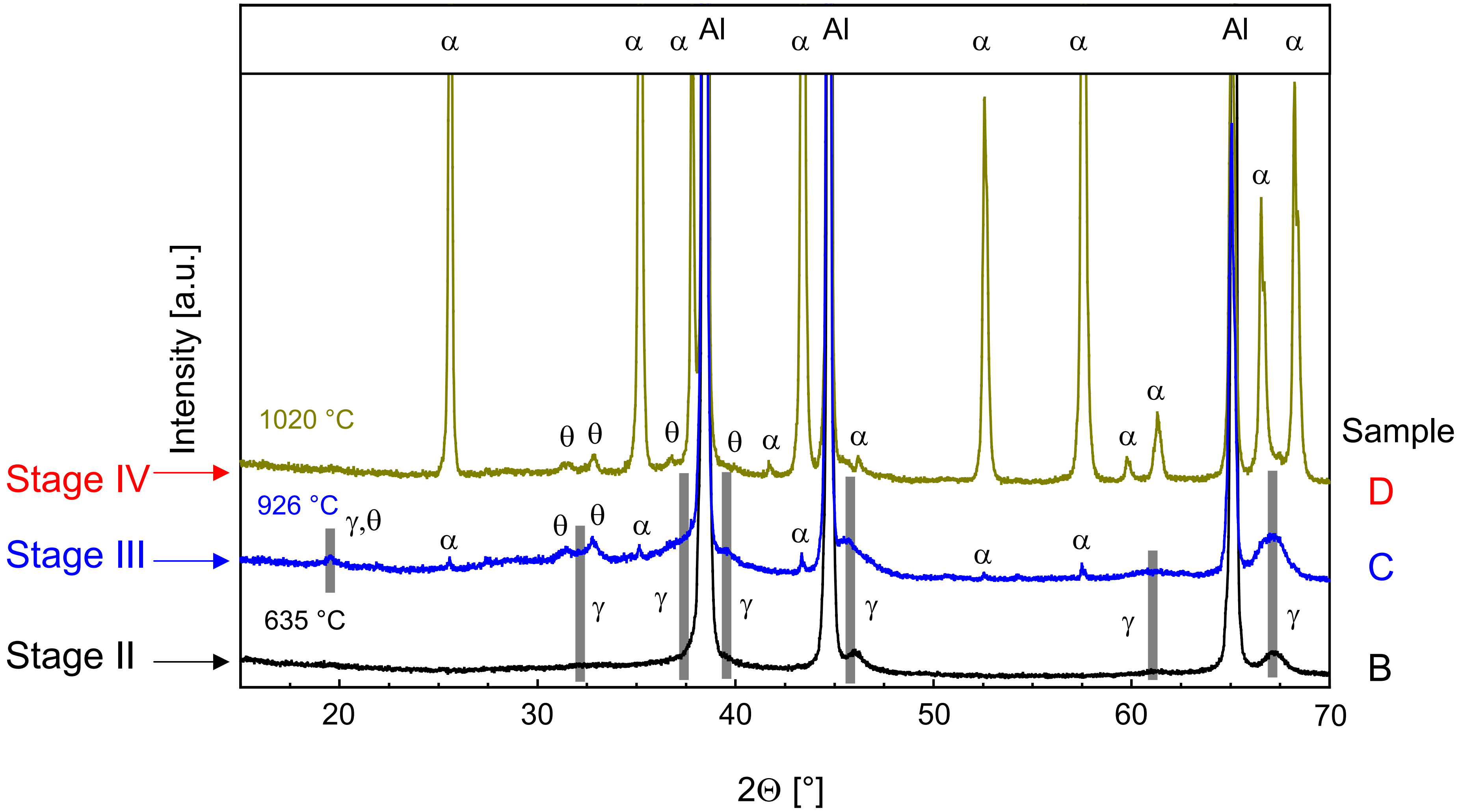
Identification of oxide phases formed at different oxidation stages



No crystalline oxide could be detected for samples recovered after first stage (point A), at 550ºC

Oxide thickness based on the measured weight increase

Powder ID	Heat. Rate, ºC/min	Estimated oxide thickness, nm			
		End of Stage I	End of Stage II	End of Stage III	Stage IV (1450 ºC)
Flakes -325 Mesh	5	7.4	27.8	N/A, near complete oxidation	
	10	8.9		N/A, ignition	
Spheres 3-4.5 mm	5	5.2	20.0	213	707
	10	3.8	18.1	202	567
	20	3.6	16.6	197	480
	40	3.9	15.2	192	395
Spheres 10-14 mm	5	4.7	17.2	176	613
	10	4.2	16.3	168	478
	20	4.6	15.4	155	379
	40	4.0	13.8	149	287

Characteristic crystallite of γ-Al_2O_3

Close to reported critical thickness of amorphous oxide

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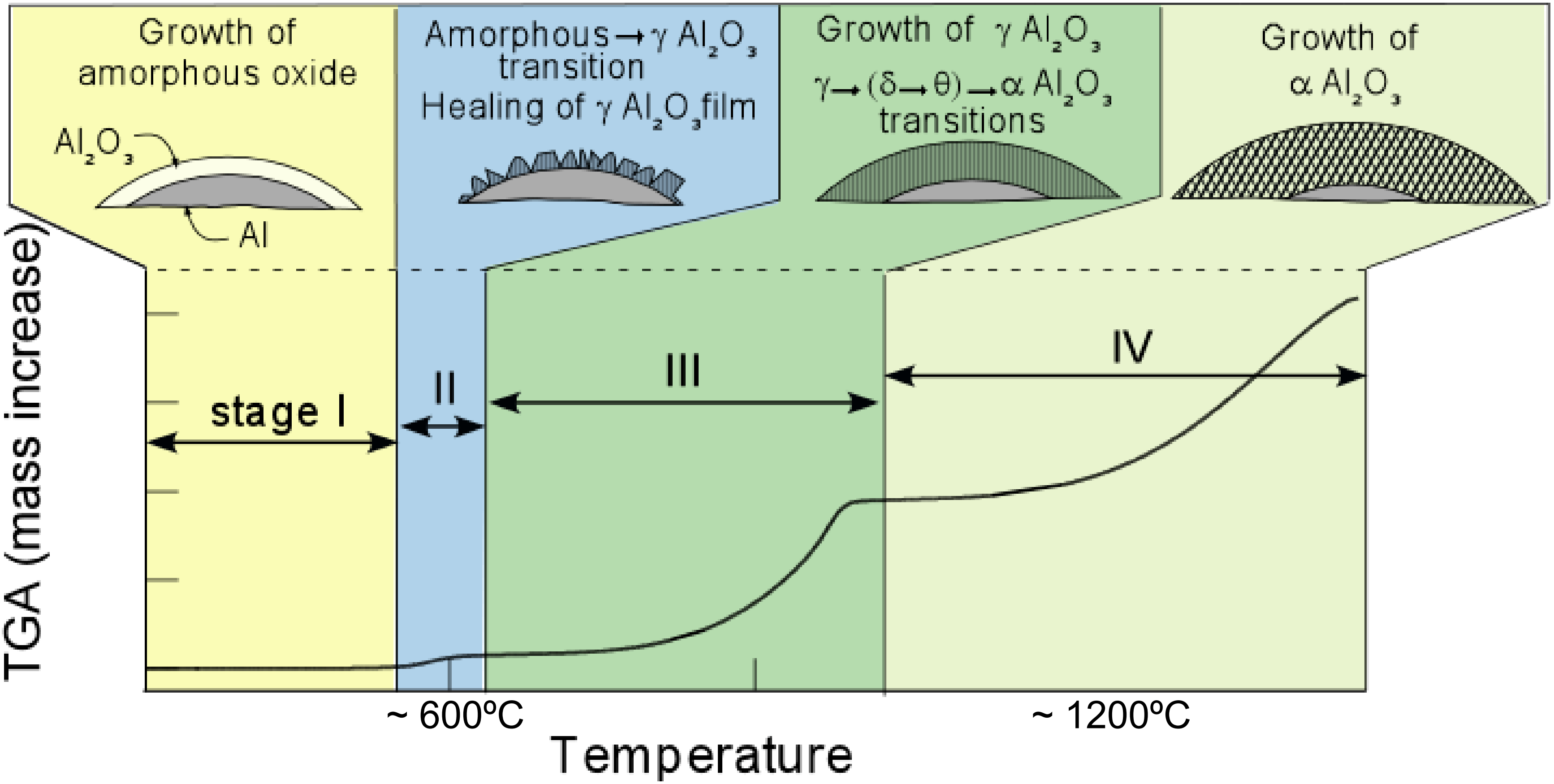
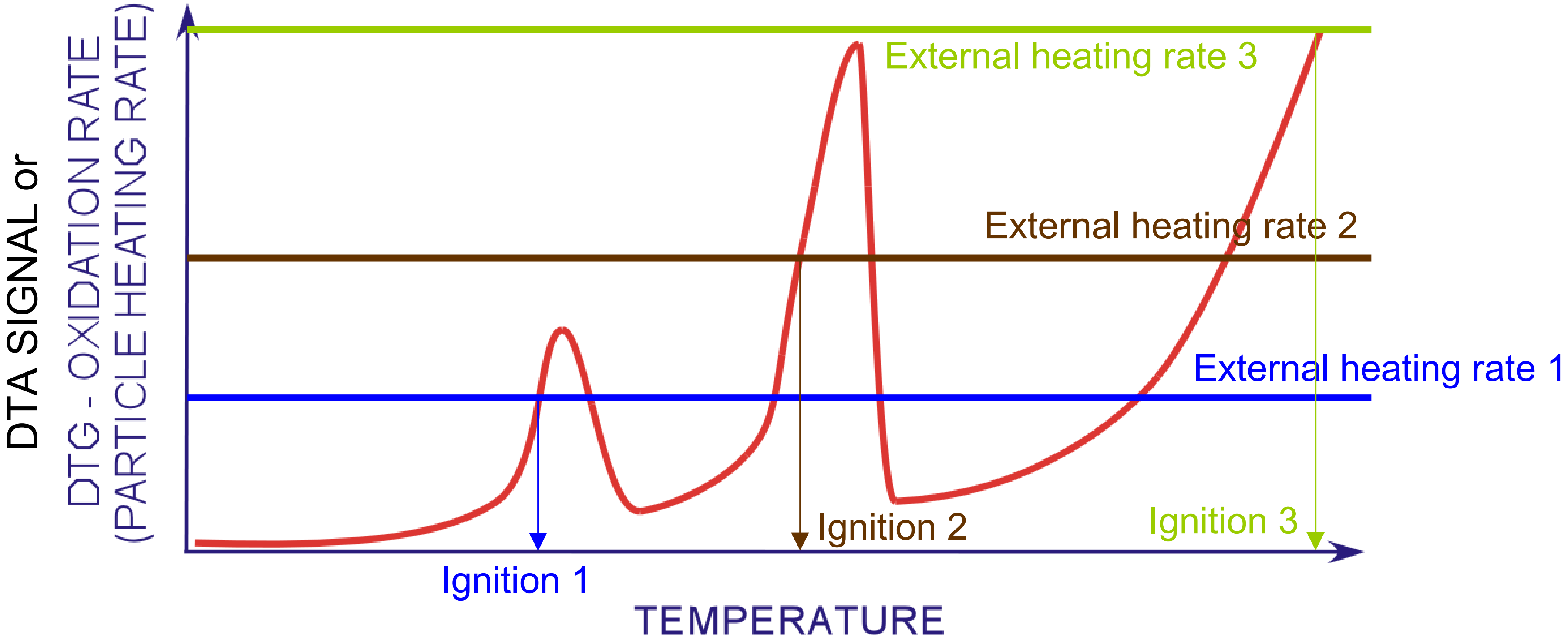
Aluminum powder oxidation processes



Modeling aluminum particle ignition

- Classic model introduces a “critical ignition temperature” as the temperature of environment in which particle ignites
  - Particle heat release rate is compared to the heat losses
  - If the heat release exceeds the losses, the particle temperature increases
  - When a pre-determined temperature is reached, particle ignites
- This model does not describe ignition in systems with rapidly changing temperatures
  - While being introduced in the flame, the particle is heated continuously
  - Ignition delay critical for many applications cannot be described
- To describe ignition of solid fuel particles in practical systems, temperature histories of **inert and reactive particles can be compared**
- A rate of self-heating due to oxidation can be compared to the rate of external particle heating

Role of aluminum self-heating in particle ignition



- Oxidation rate peaks at least three times during the particle heating
- Ignition can occur at one of these three peaks, depending on the specific heat transfer conditions
- For the same heating rate, ignition can occur at different temperatures for particles of different sizes

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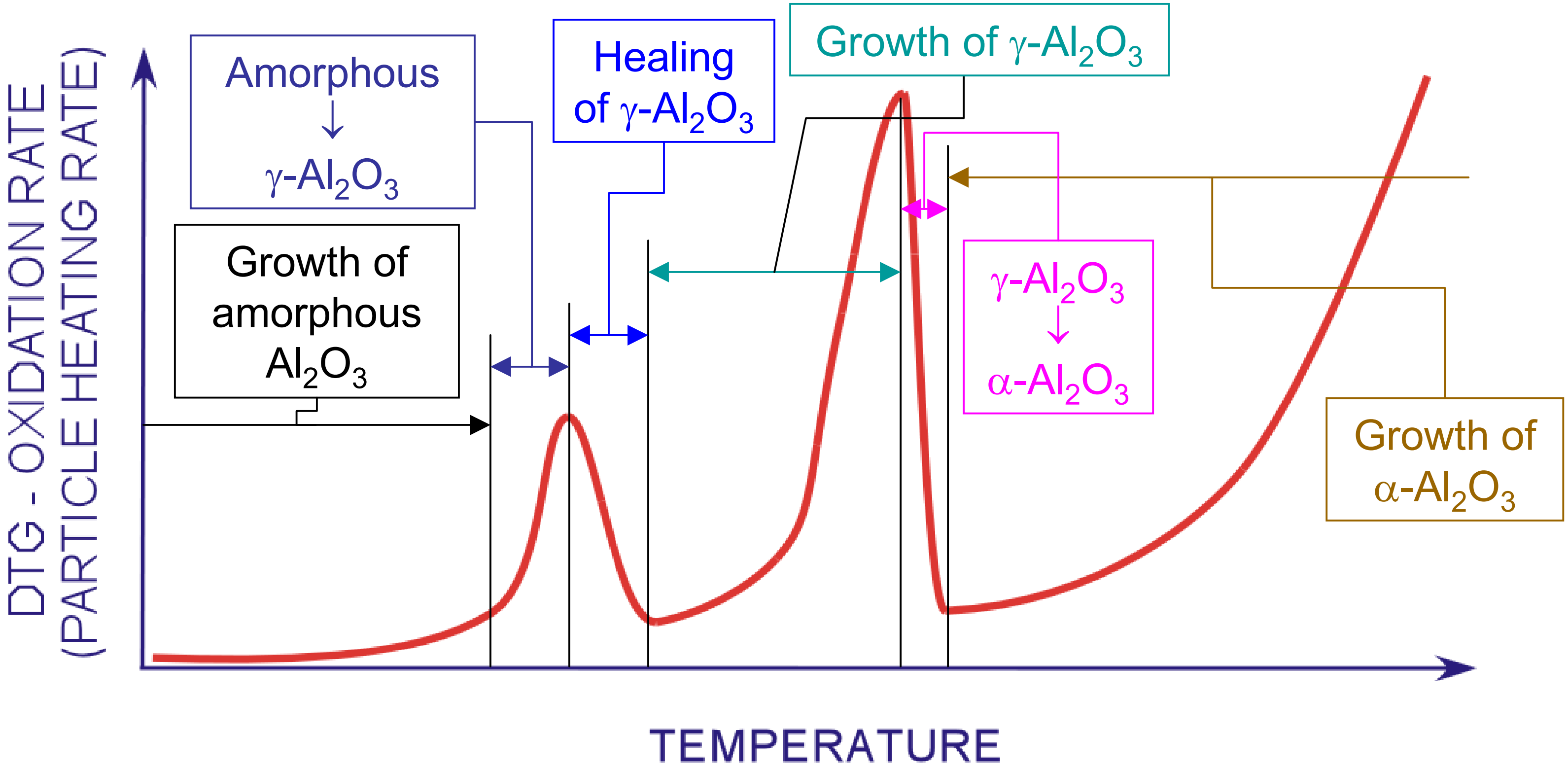
Modeling of self-heating using the oxidation mechanisms



- Rate of each process occurring during particle oxidation needs to be identified
- The transitions between different oxidation stages need to be described quantitatively

Model development: work in progress

- Rates of **growth** of different Al_2O_3 polymorphs are determined from TGA measurements
- The rates are **consistent** for different size and morphology powders
  - spherical powders
  - non-spherical powders
  - flakes
- Found activation energies for growth of γ and α alumina agree with the activation energies reported in the literature for the rate of oxygen diffusion along grain boundaries in respective oxide layers
- A model describing kinetics of the occurring **phase transitions** is being developed and coupled with the oxide growth model
  - TGA measurements are used to determine both activation energy and pre-exponent of the phase changes
  - The thickness of oxide layer affects stability of transition alumina phases
  - **Current objective**: describe TGA curves for different size powders oxidized at different heating rates
- Once developed, the model will be used to model ignition of aluminum powders of different sizes and heated at different rates

Conclusions

- Experimental data on aluminum ignition cannot be adequately explained by:
  - Pre-set “ignition temperature”
  - Analysis of stresses developed in oxide layer
  - Growth of surface oxide considered as a single rate process
- Phase transformations between alumina polymorphs occur within the oxide layer produced by thermal oxidation of aluminum powders
- Occurring phase changes and growth of different alumina polymorphs explain the step-wise oxidation of aluminum observed by thermal analysis
- Kinetics of growth of different alumina polymorphs and kinetics of phase changes between these polymorphs need to be accounted for to model aluminum ignition: ignition temperatures can vary widely
- The necessary thermal kinetics data can be obtained from processing of the DTA experimental results

Attachment: interpreting TGA experiments

Consider growth of oxide layer thickness:

$$\frac{dh}{dt} = \frac{C}{h}\exp\left(-\frac{E_a}{RT}\right) \qquad (1)$$

Where h is oxide thickness
E_a is activation energy
m_0 is initial sample weight; m is experimental sample weight (from TGA)
C is a constant

For a flat surface, the oxide scale thickness is

$$h \sim \left(\frac{m}{m_0} - 1\right) \qquad (2)$$

The change of oxide thickness

$$\frac{dh}{dt} \sim \frac{dm}{dt} \qquad (3)$$

Substitute (2) and (3) in (1), we obtain

$$\left(\frac{dm}{dt}\right) = \frac{C^*}{m/m_0 - 1}\exp\left(-\frac{E_a}{RT}\right) \qquad (4)$$

An Arrhenius-type equation is obtained. A slope of the straight line can be used to determine the activation energy

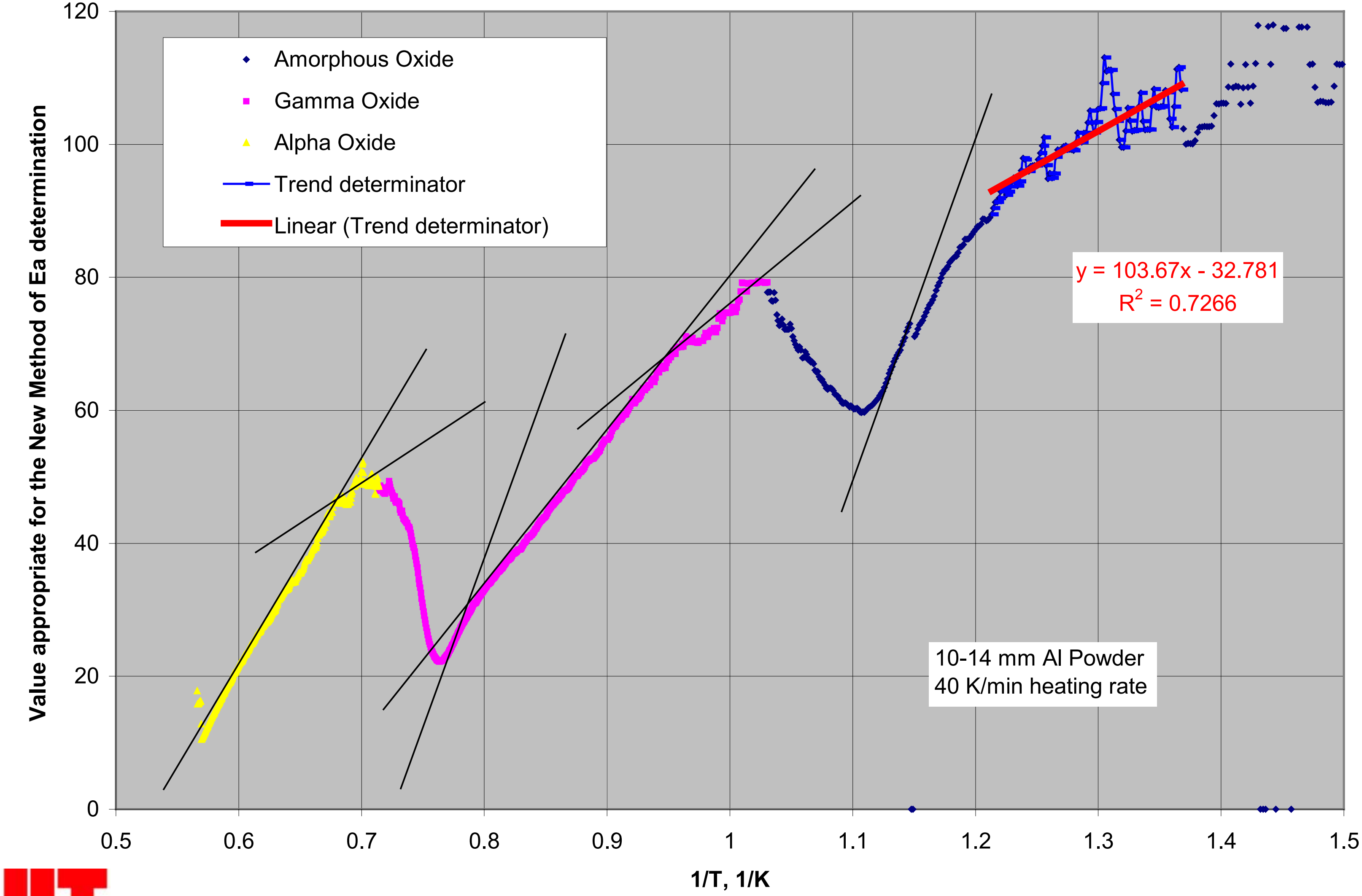
$$\ln\left(\frac{dm}{dt}\right) + \ln\left(\frac{m}{m_0} - 1\right) + C^{**} = -\frac{E_a}{RT} \qquad (5)$$

DTG curve

TG curve

Attachment: TGA experiment processing

Each oxidation stage characterized by the growth of a specific Al_2O_3 polymorph can be described by a straight line: respective activation energies can be found



Ignition and Combustion of Nanocomposite Al/MoO_3

Prof. Michelle Pantoya
Daniel Prentice, Dustin Osborn,
Kevin Moore, John Granier,
Randy White, Matt Jackson,
Emily Hunt

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COMBUSTION
Mechanical Engineering

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Dr. David Mann
US Army ARDEC, Mr. Steve Nicolich
Los Alamos National Lab, Dr. Steve Son

Objectives

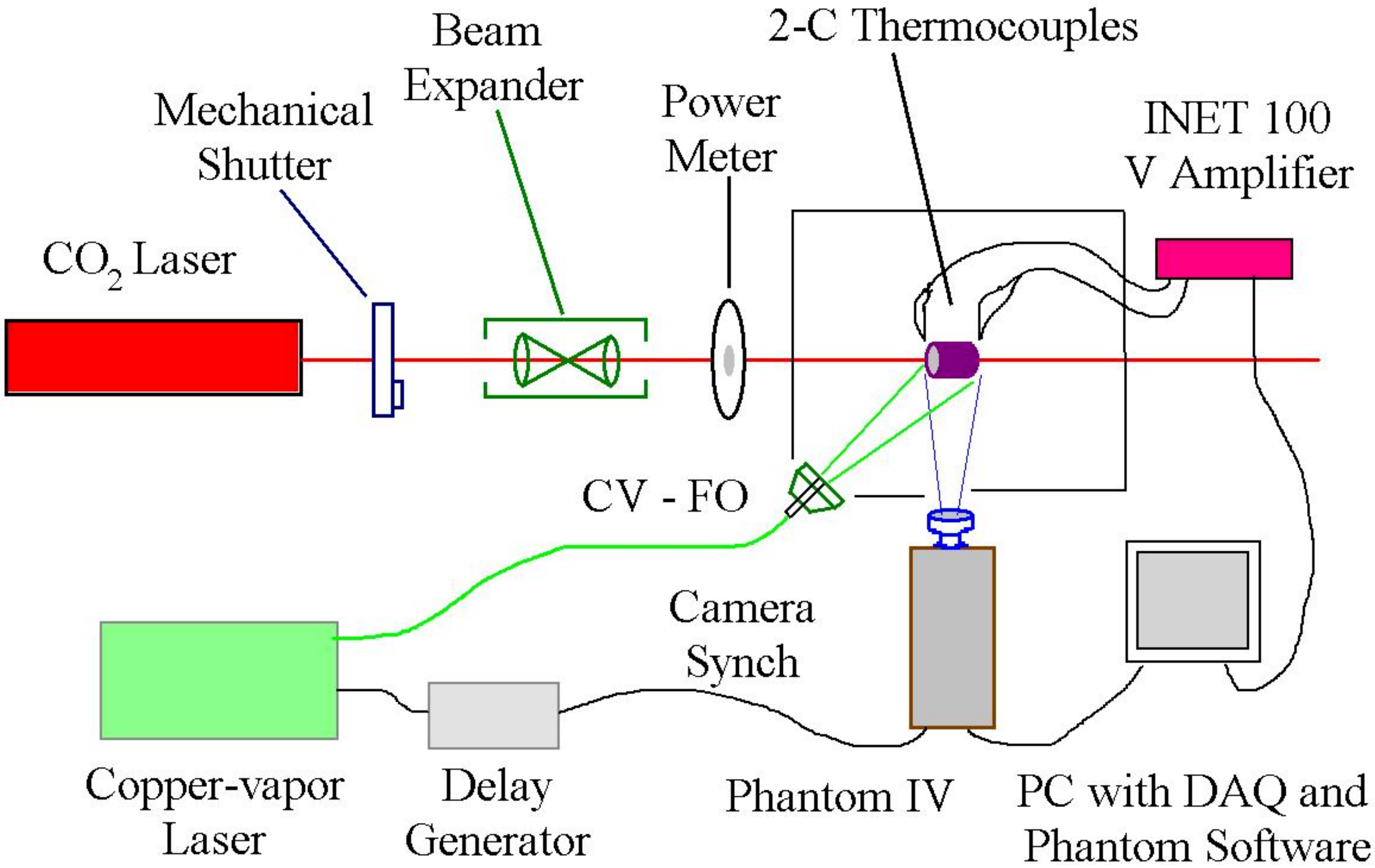
Understand unique behaviors of nano vs traditional micron composite thermites

I. Explore thermal ignition sensitivity and burning behavior as a function of:
- reactant particle size (nm to μm)
- composition (fuel rich to fuel lean, additives and binders)
- bulk density (5 – 75 % TMD)

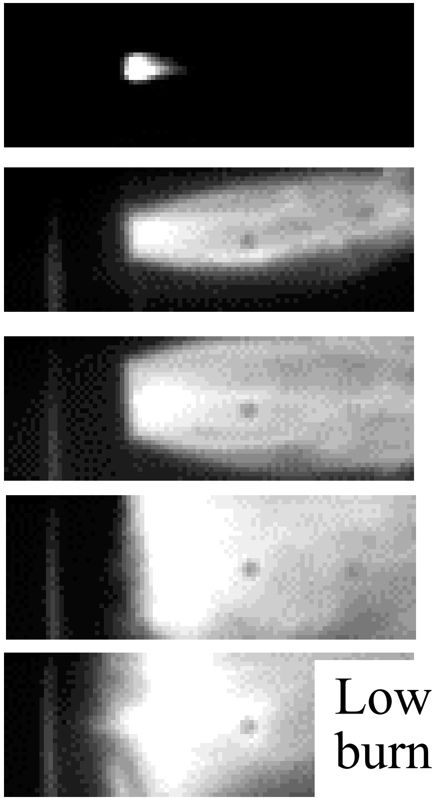
↳ II. Develop models to describe ignition and propagation in nanocomposite materials.

↳ III. Transition research into applications relevant to the DoD.

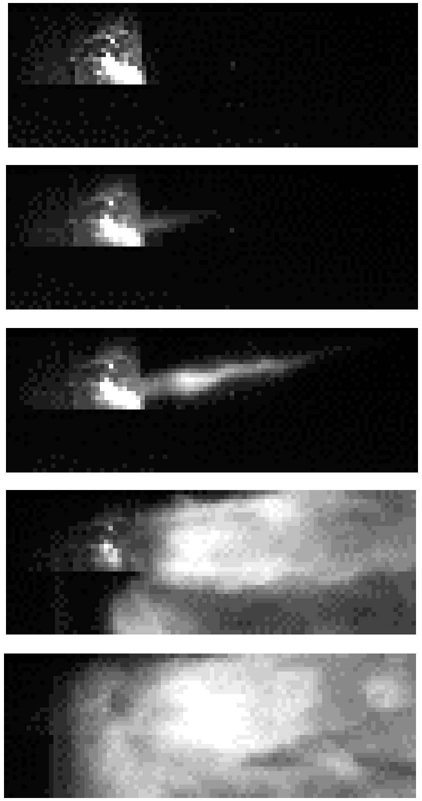
Ignition & Flame Propagation



Imaging highly luminescent reactions



Low light transmission burn sequence:
no cv laser, 32 f stop,
2 ND filters allow 2.5% transmission



Split image of the CV laser coupled with the camera
Camera scans individual lines of the CCD from the bottom up.
Each image is 128 by 32 pixels.
The CV strobe is delayed such that illumination is only provided after the first 16 lines are scanned.

the laser light reflects off of the solid/gas cloud

Ignition time and burn rate measurements

High-Speed Imaging up to 100,000 fps

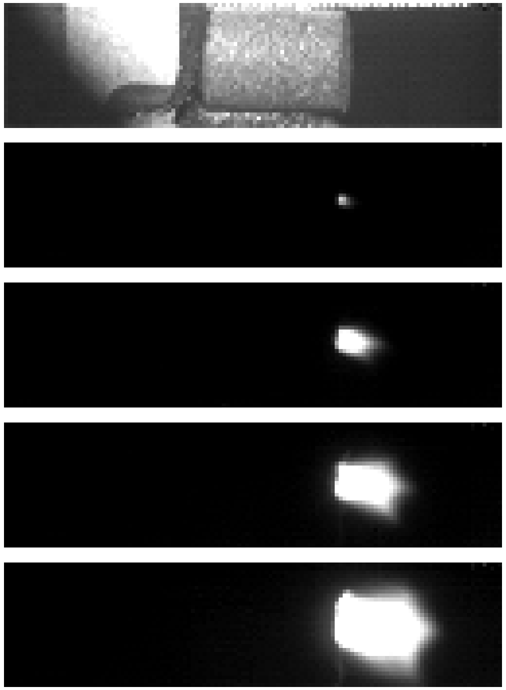


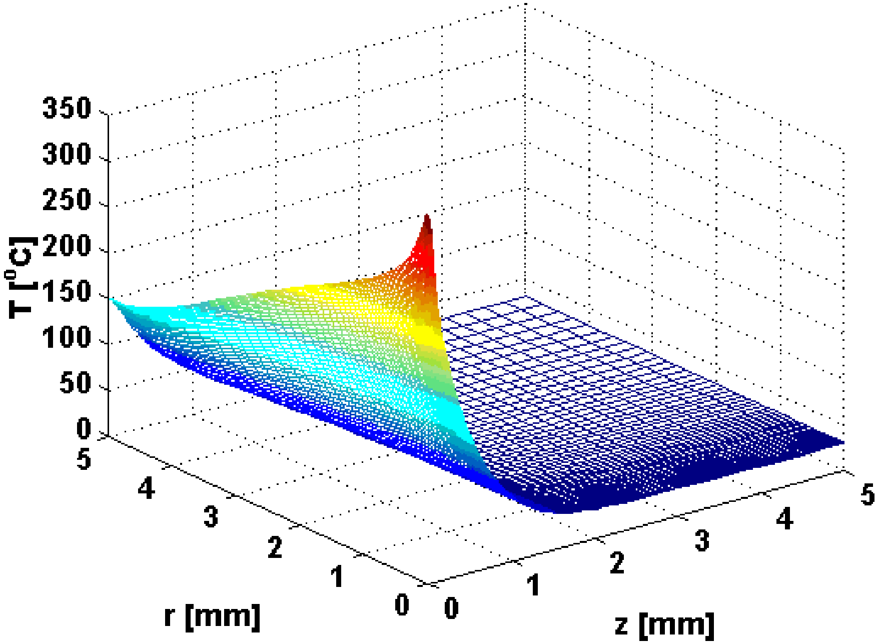
Image 0
0.0 s

1109
+34 ms

1110
+31.5/31.5 μs

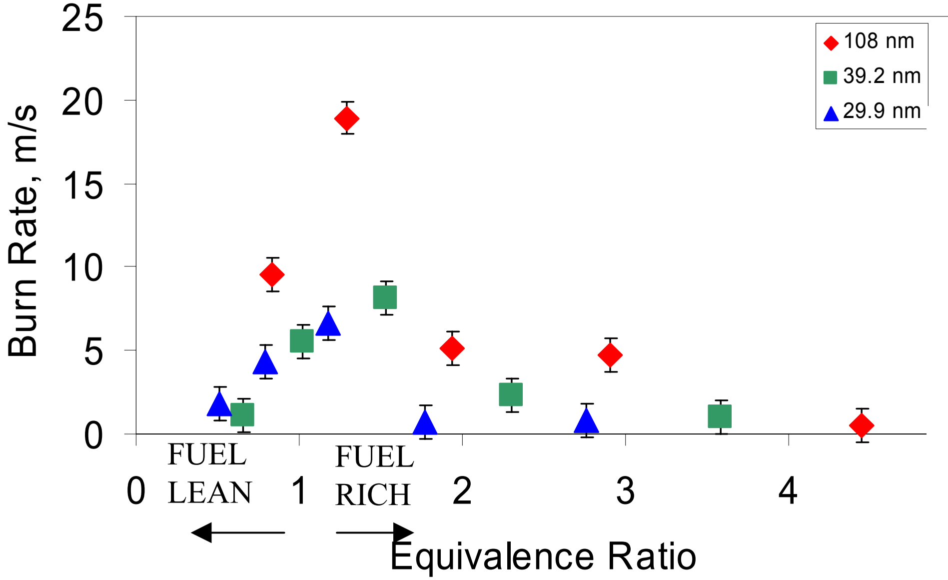
1111
+31.5/63.0 μs

1112
+31.5/94.5 μs

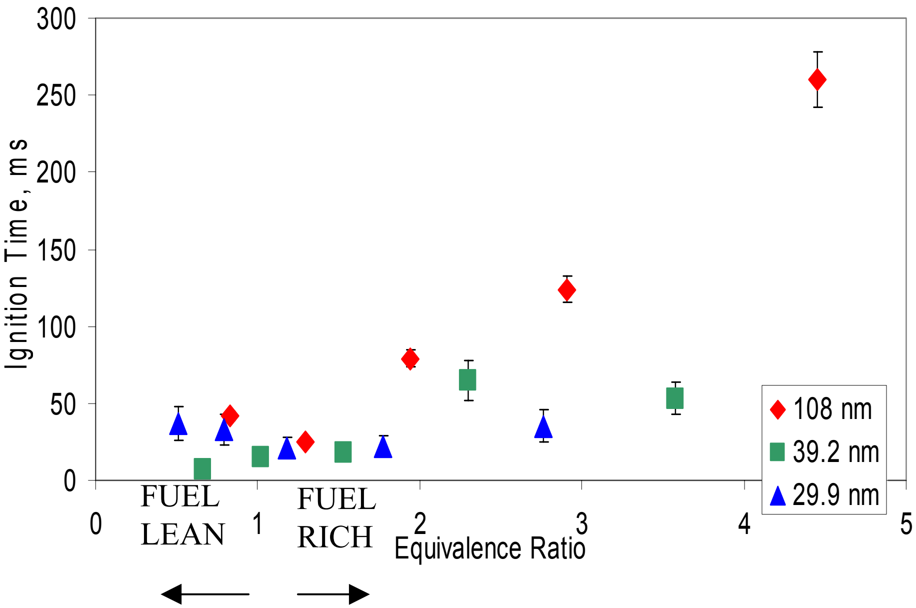


- Entire front face of pellet is exposed to Gaussian laser beam
- Ignition starts in the center (hot spot formed)
- Propagation both radially and axially

Al+MoO$_3$ Ignition Study



Burn rate and ignition time are a function of composition

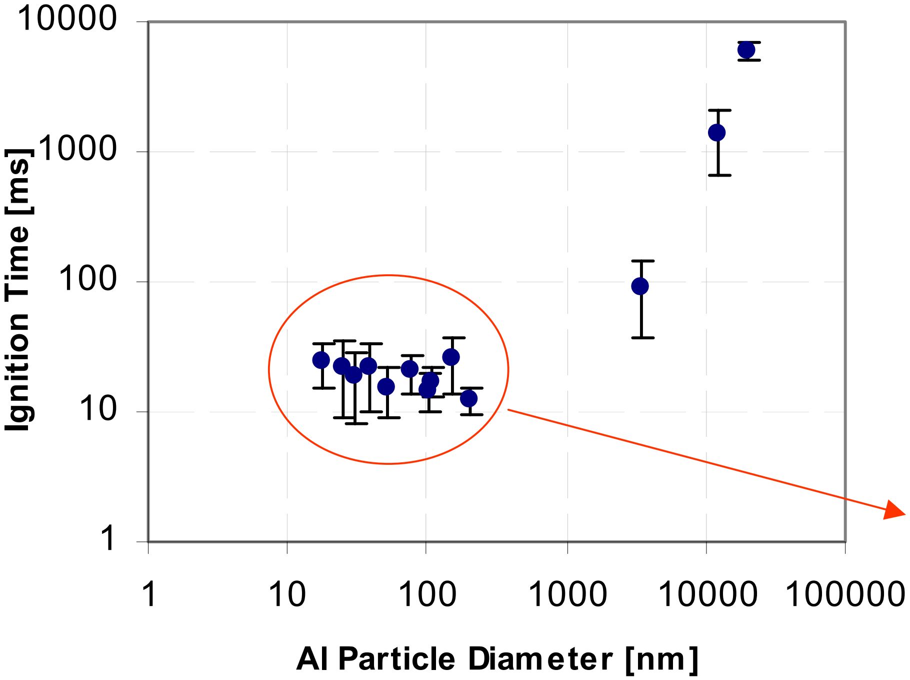


- TMD fixed at 40%
- Al reacts with the solid oxidizer *and* air.
- The increased Al in a fuel rich mixture improves conductive heat transfer.

$$2\mathrm{Al} + \mathrm{MoO}_3 \rightarrow \mathrm{Al}_2\mathrm{O}_3 + \mathrm{Mo}$$

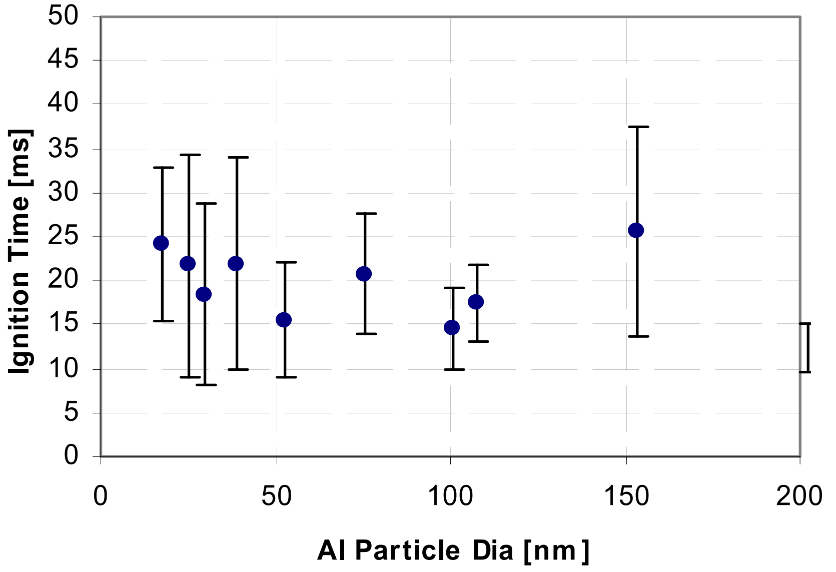
$$\phi = \frac{\left(F/A\right)_{ACT}}{\left(F/A\right)_{ST}}$$

Al+MoO_3 Ignition Study



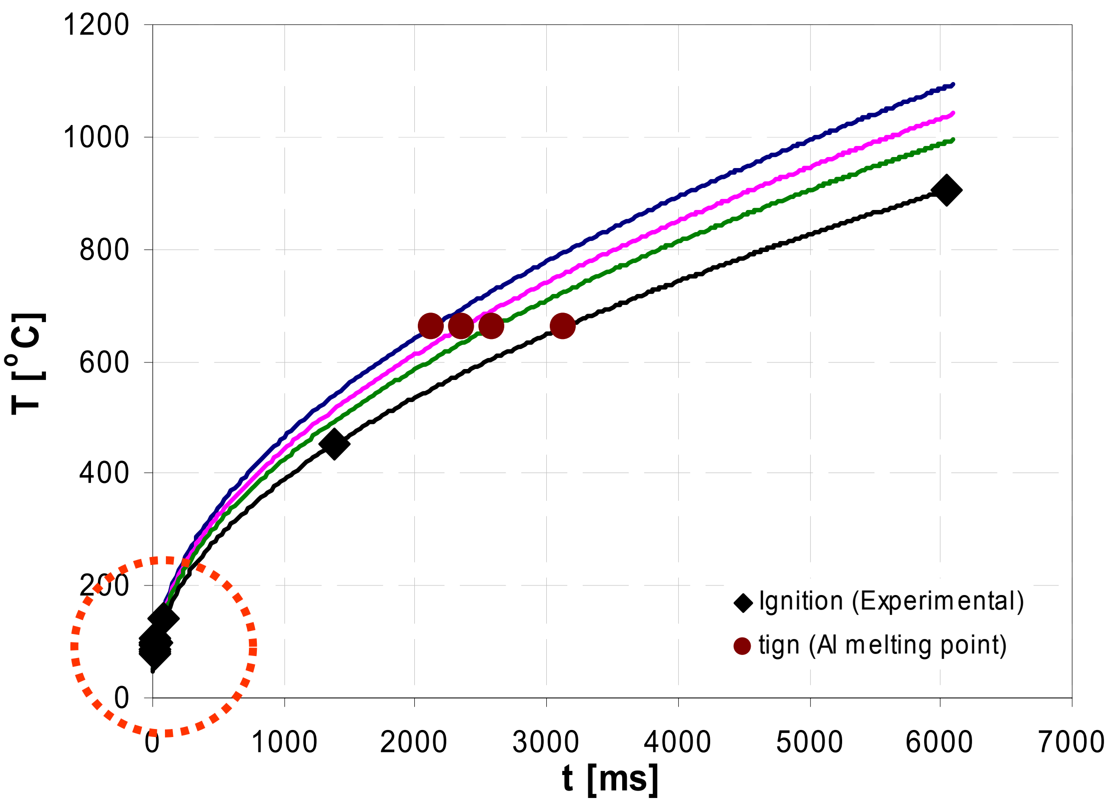
Granier and Pantoya, Comb. Flame 2004

- Nano-Al reduces time to ignition by two orders of magnitude!
- Diffusion reactions: particle size dependant melting temperature may contribute to the reduced ignition times



- Absorption properties of nanomaterials may induce thermal non-equilibrium *(Dlott and co-workers)*

Inert heating to ignition time



$$\frac{\partial T}{dt} = \alpha \frac{\partial^2 T}{dx^2}$$

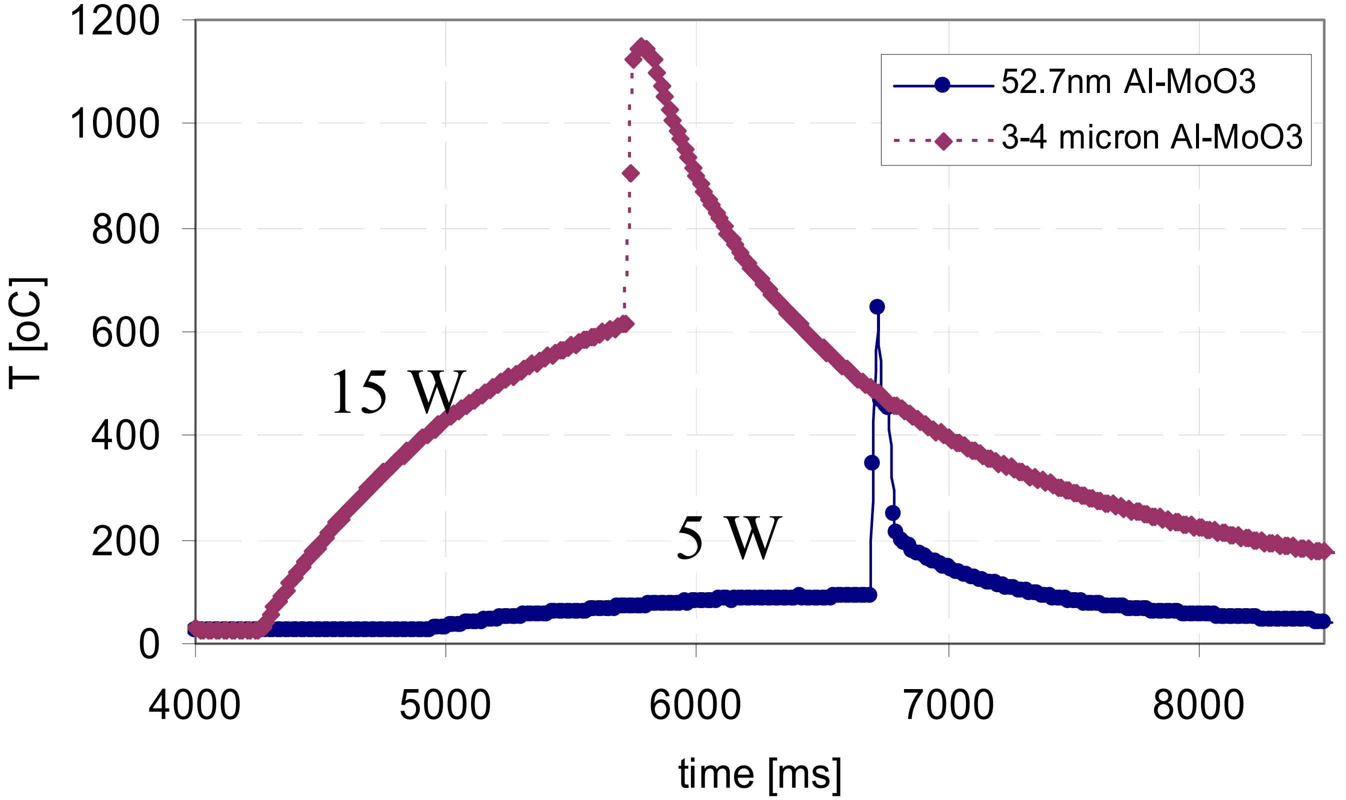
$$T_{x=0,r=0} = T_i + \frac{2q_o''\sqrt{\alpha t/\pi}}{\mathrm{k}}$$

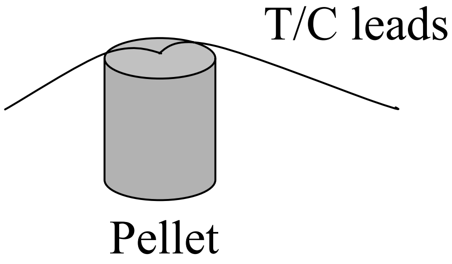
Measured ignition times for nanocomposites correspond with calculated ignition temperatures far below the bulk melting temperature for Al.

Mechanical Engineering Dept.

Al+MoO_3 Ignition Study

75-µm C-type thermocouple held by spring tension of the wire leads.

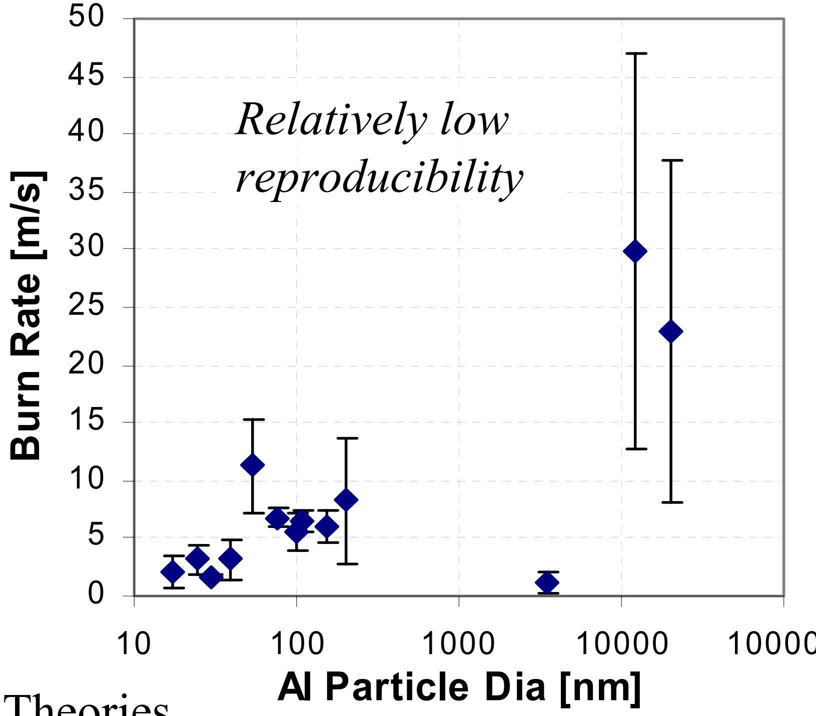


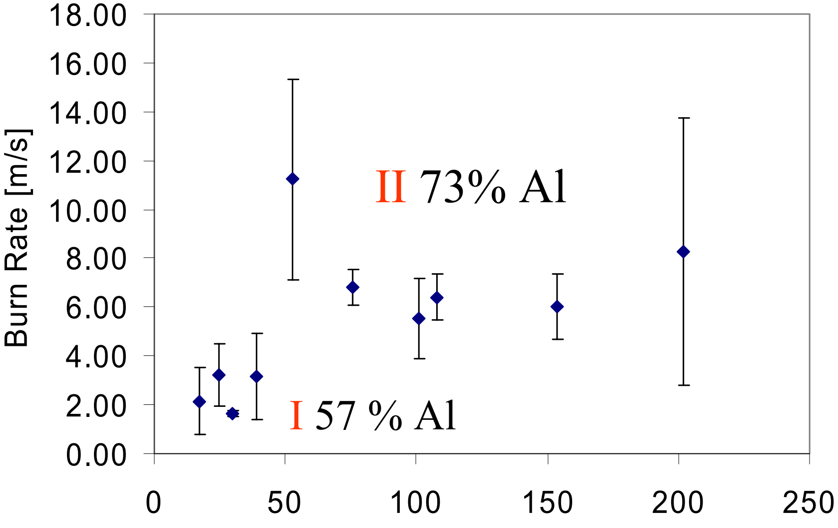


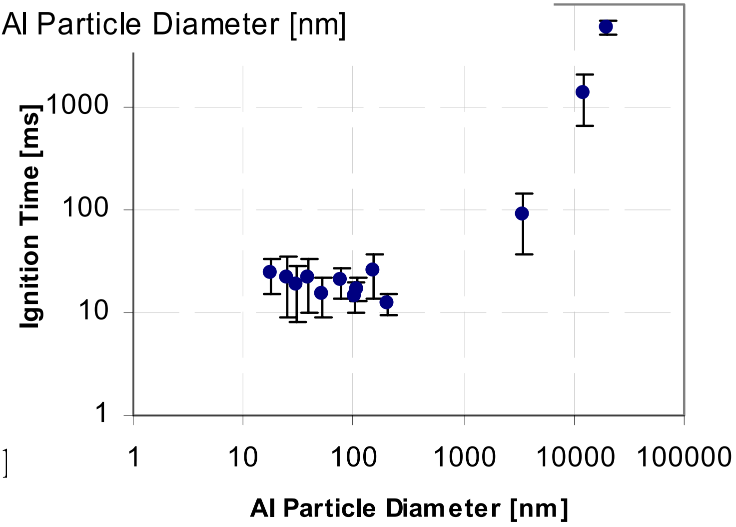
Ignition occurs at a lower temperature in the nanocomposite

Mechanical Engineering Dept.

Combustion Wave Speed





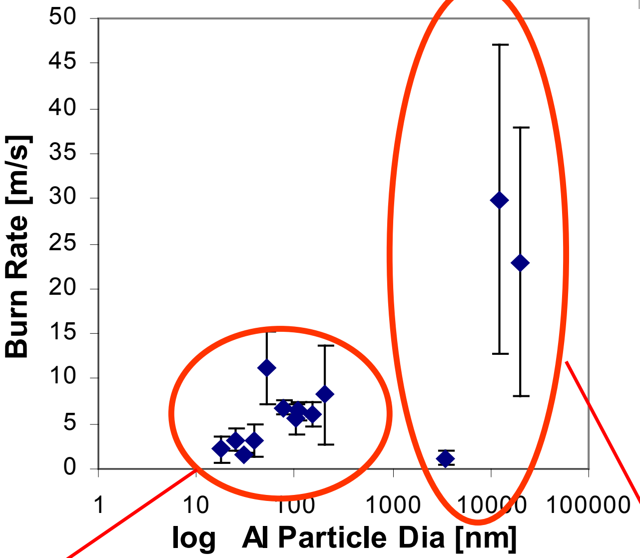


Theories

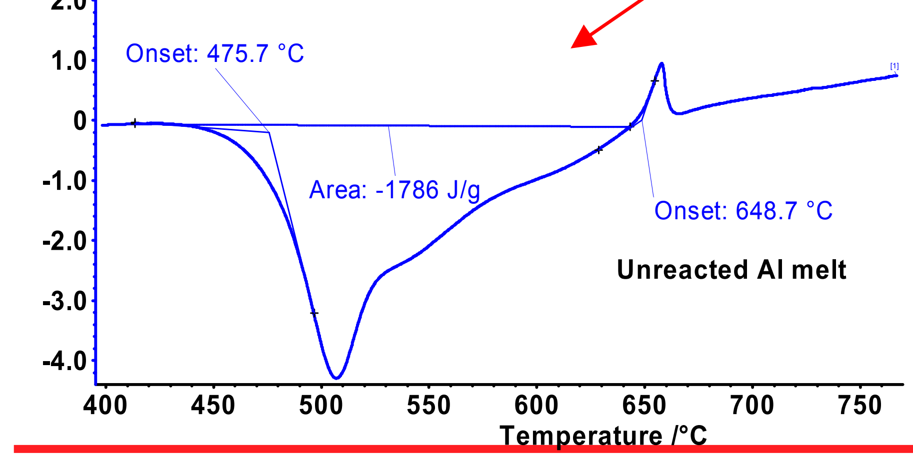
- Preheated Micron Composites
- Increased Al_2O_3 creates lower conductivity in nanocomposites
- Diffusion reaction drastically effected by the phase (sol liquid, gas) of reactants

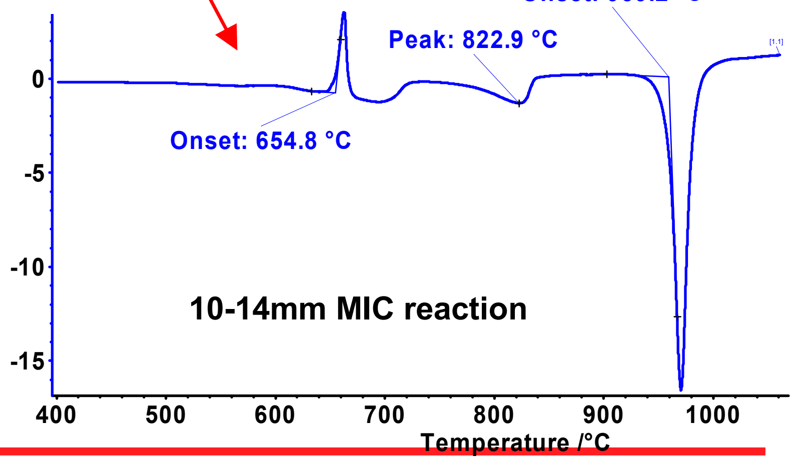
Micron- to Nano- Burning Behavior Dependent on Initial State

Slower Nano-composites react prior to phase transition of either Al or MoO_3

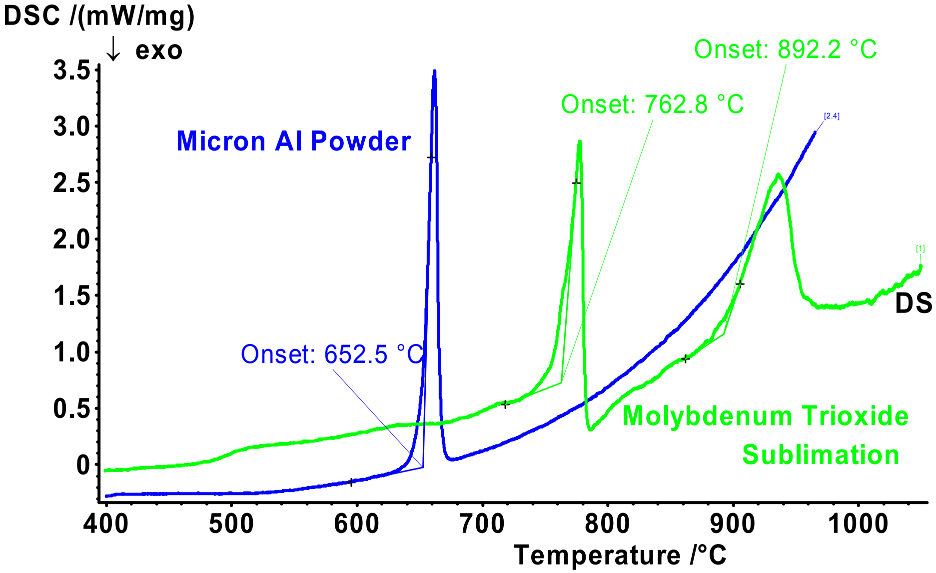


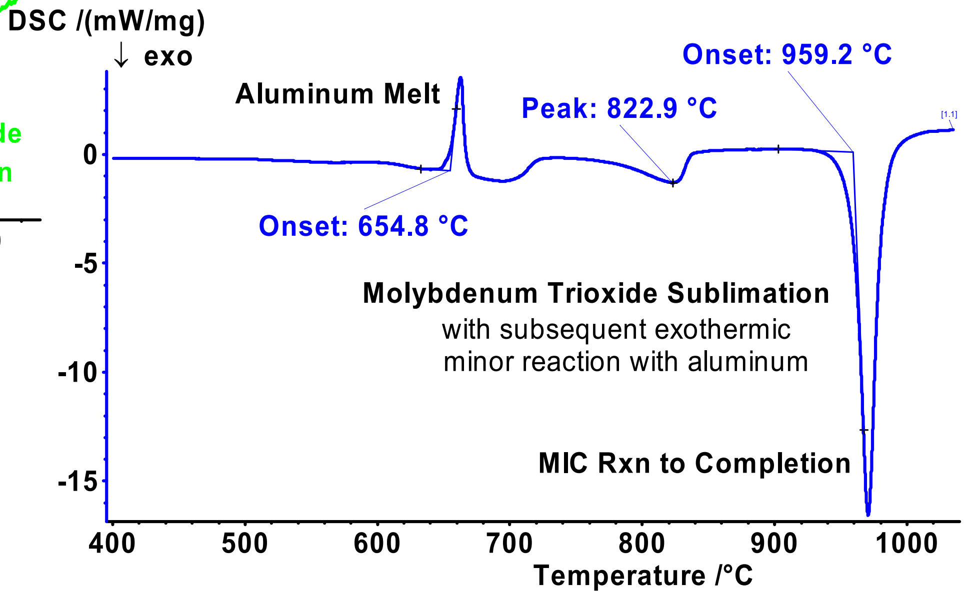
Faster Micron-composites react after phase transition of both Al and MoO_3





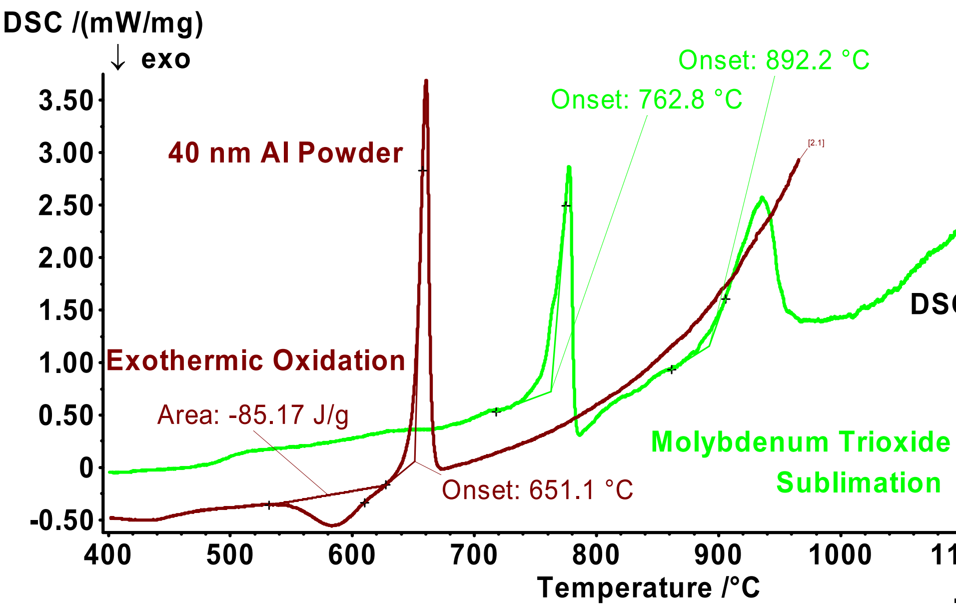
Micron MIC DSC Results



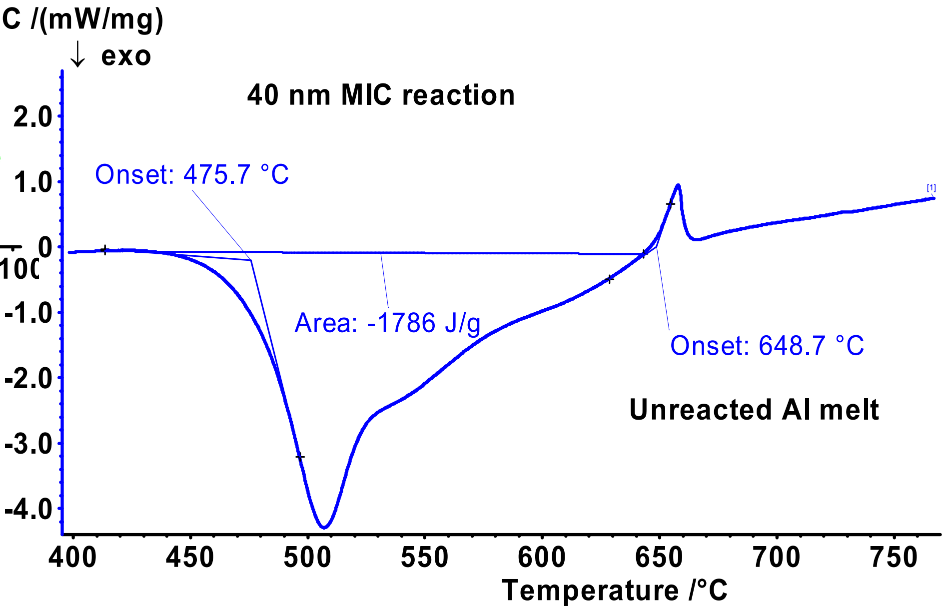


Aluminum melting and MoO_3 sublimation occur before micron MIC "reacts"

Nano MIC DSC Results



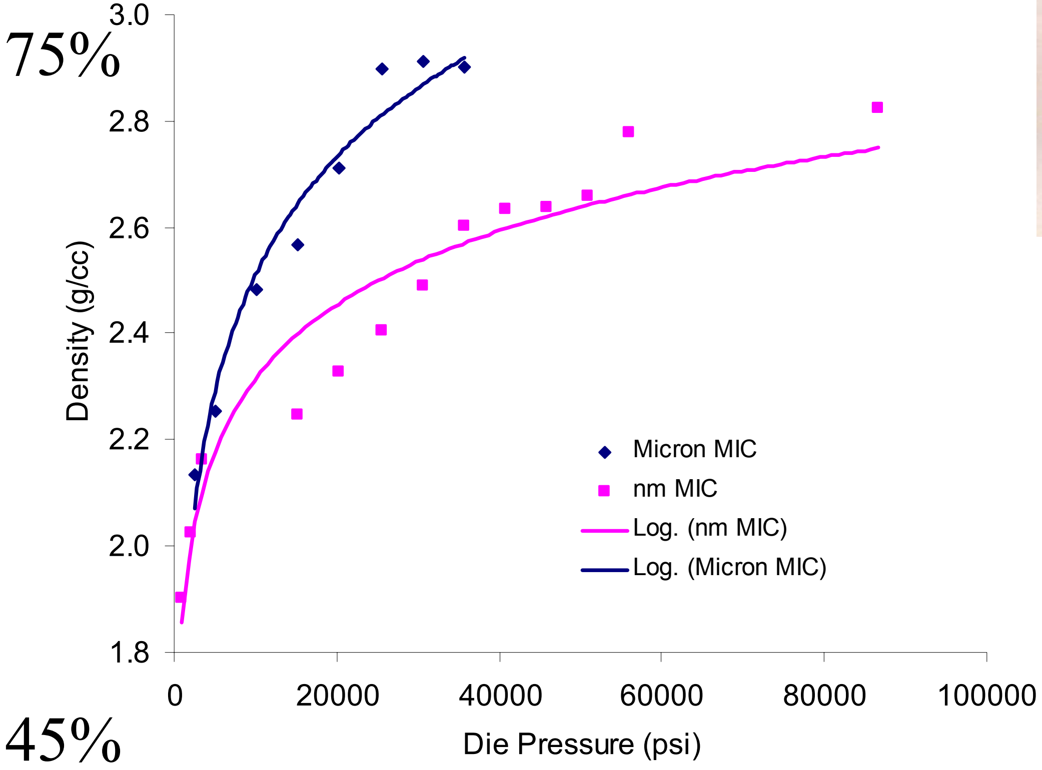
Nano MIC is a completely new reaction timing mechanism

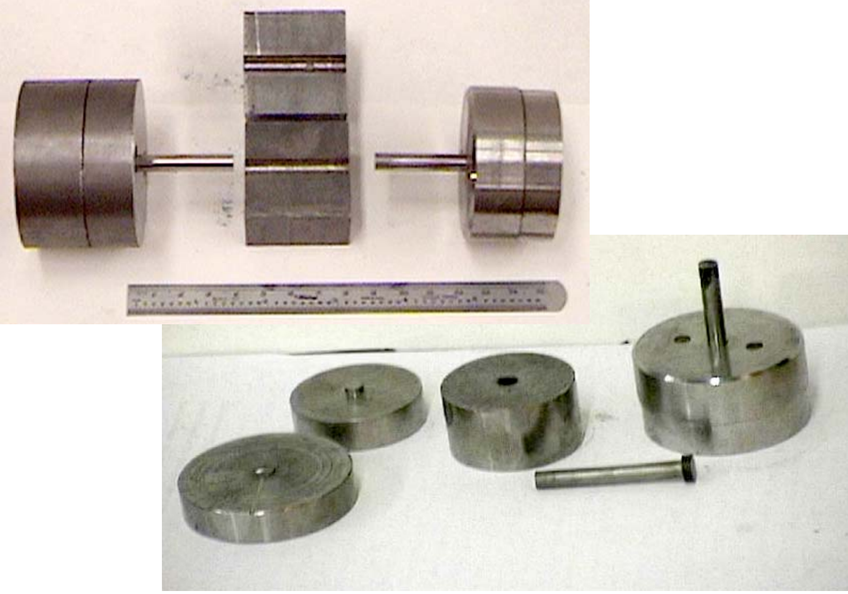


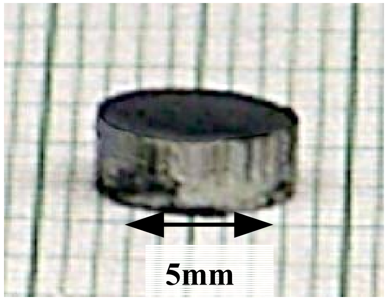
Reactants are in solid-solid phase – justifying slower heat propagation and diffusion reaction rates

The role of density on burning performance

Easier to press micron-materials

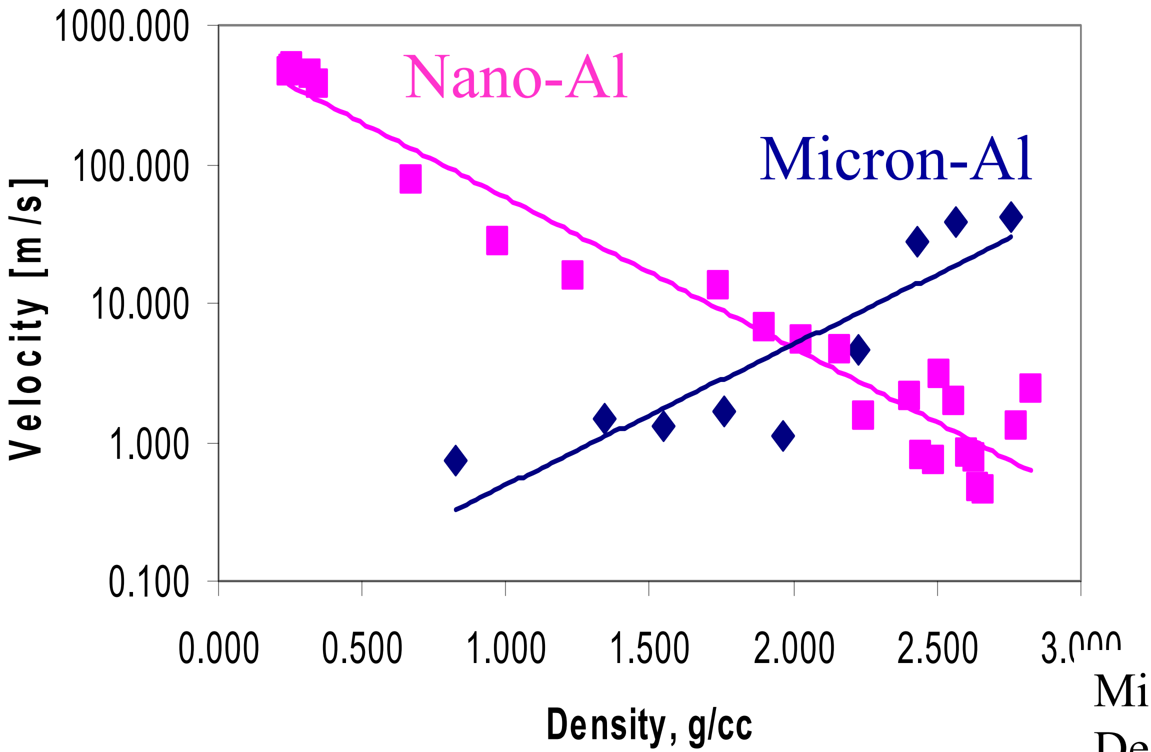






Nano powders are naturally porous – more force is required to eliminate the powder gaps

Effect of Bulk Density on Compact Powder Burn Velocity



Nano Al is unique from the micron Al in that it easily oxidizes in gaseous air

The exothermic oxidation may be the initiating step for the nanocomposite reaction

What is causing these unique behaviors?

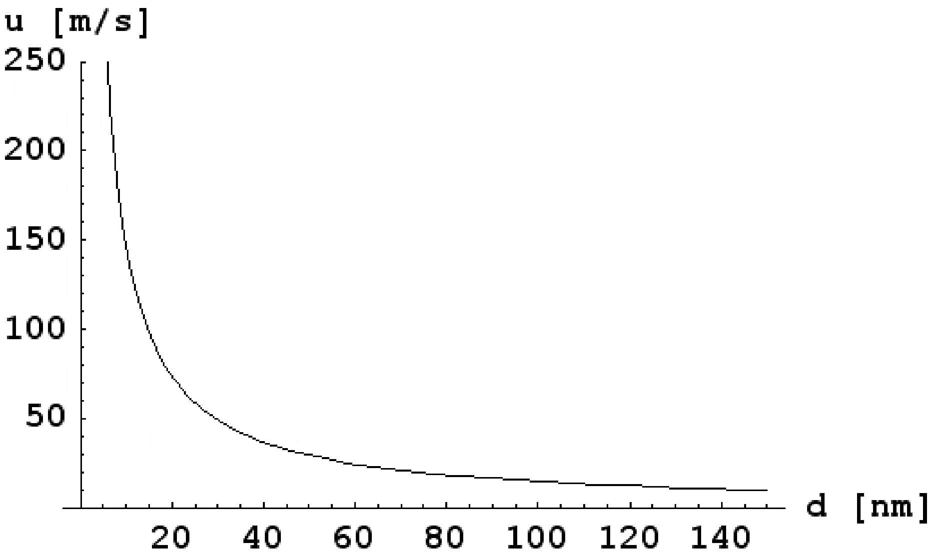
- Increasing density (decreased pore sizes) reduces gaseous air volume and air concentration in both micron and nano composites

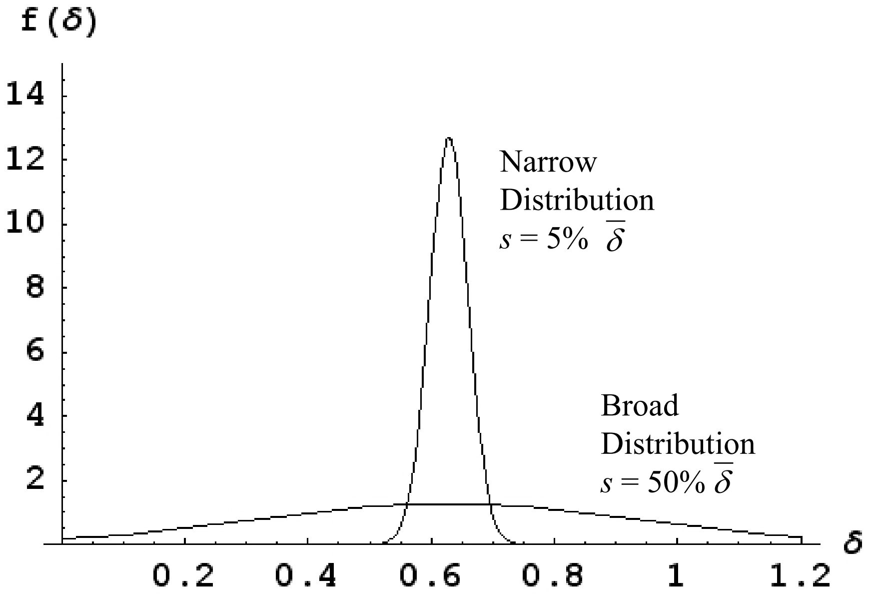
Micron
Decreasing air volume = Increasing k_{eff}

Nano
Decreasing air concentration =
Decreasing Al oxidation path

Mechanical Engineering Dept.

Velocity: effect of particle size distribution





$$u(\delta) = \sqrt{12 \frac{A_* \exp\left(\frac{-E_A}{RT_f}\right)\left(\frac{RT_f}{E_A}\right)\alpha^2}{(\delta d_{\max})^2 \frac{T_f - T_o}{T_f}}}$$

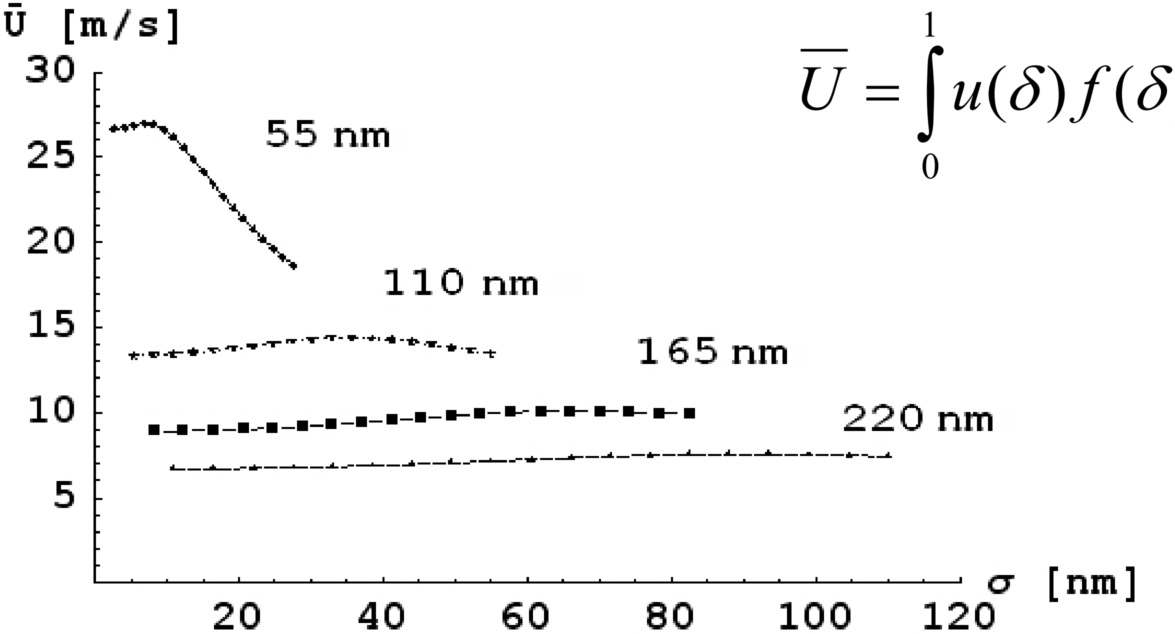
$$f(\delta, s) = \left(\frac{1}{s\sqrt{2\pi}}\right)\exp\left[-\frac{1}{2}\left(\frac{\delta - \bar{\delta}}{s}\right)^2\right]$$

$$\bar{\delta} = {d_{avg}}/{d_{\max}} \qquad \delta = {d}/{d_{\max}} \qquad s = {\sigma}/{d_{\max}}$$

Assumes diffusive mechanisms are dominant

Armstrong, R. *Combustion Science and Technology* v. 71, pp. 155-174 (1990).

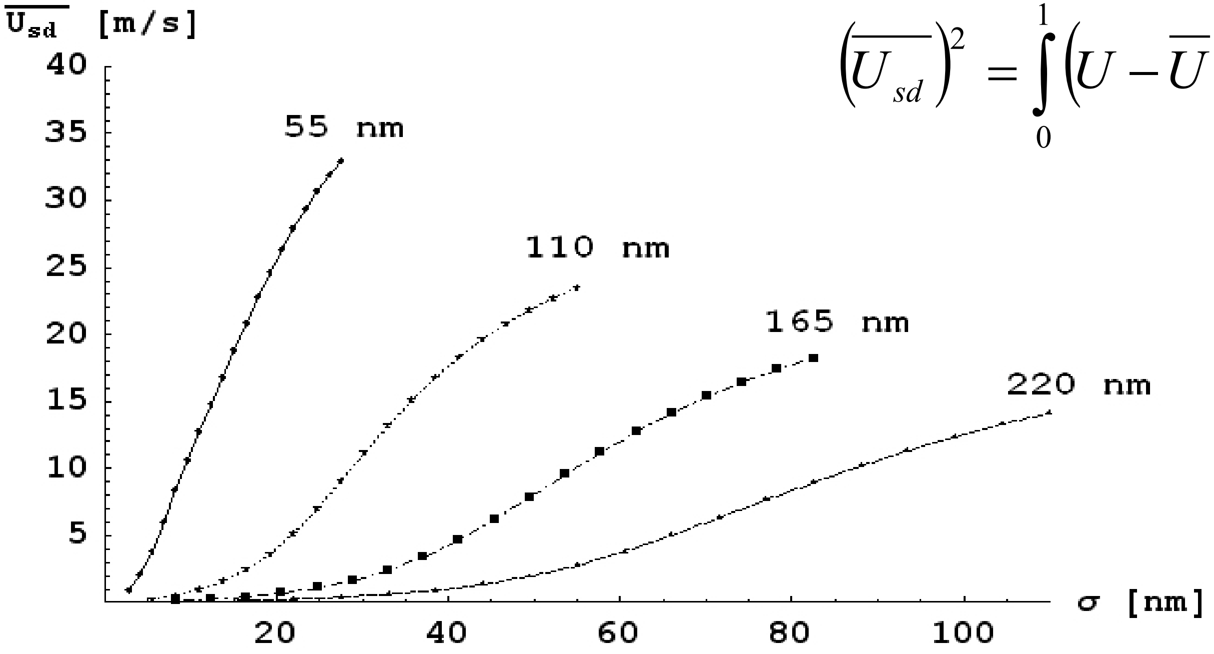
Burn rate sensitivity on size distribution



$$\overline{U} = \int_0^1 u(\delta) f(\delta) d\delta$$

- Particle diameters greater than 100 nm remain unaffected by size distribution.
- Behavior results from the increased sensitivity of *d* on the calculation of burn rate.
- Knowledge of the size distribution for particles smaller than 100 nm is important for reproducing a burn rate measurement.

Size distribution and reproducibility



$$\left(\overline{U_{sd}}\right)^2 = \int_0^1 \left(U - \overline{U}\right)^2 f(\delta)\, d\delta$$

- $\overline{U_{sd}}$ increases as the size distribution becomes more broad.
- Results suggest that nano-materials with narrow size distributions will enhance the repeatability in the combustion performance.

Bimodal: background

- Ultrafine Al + micron Al + Air

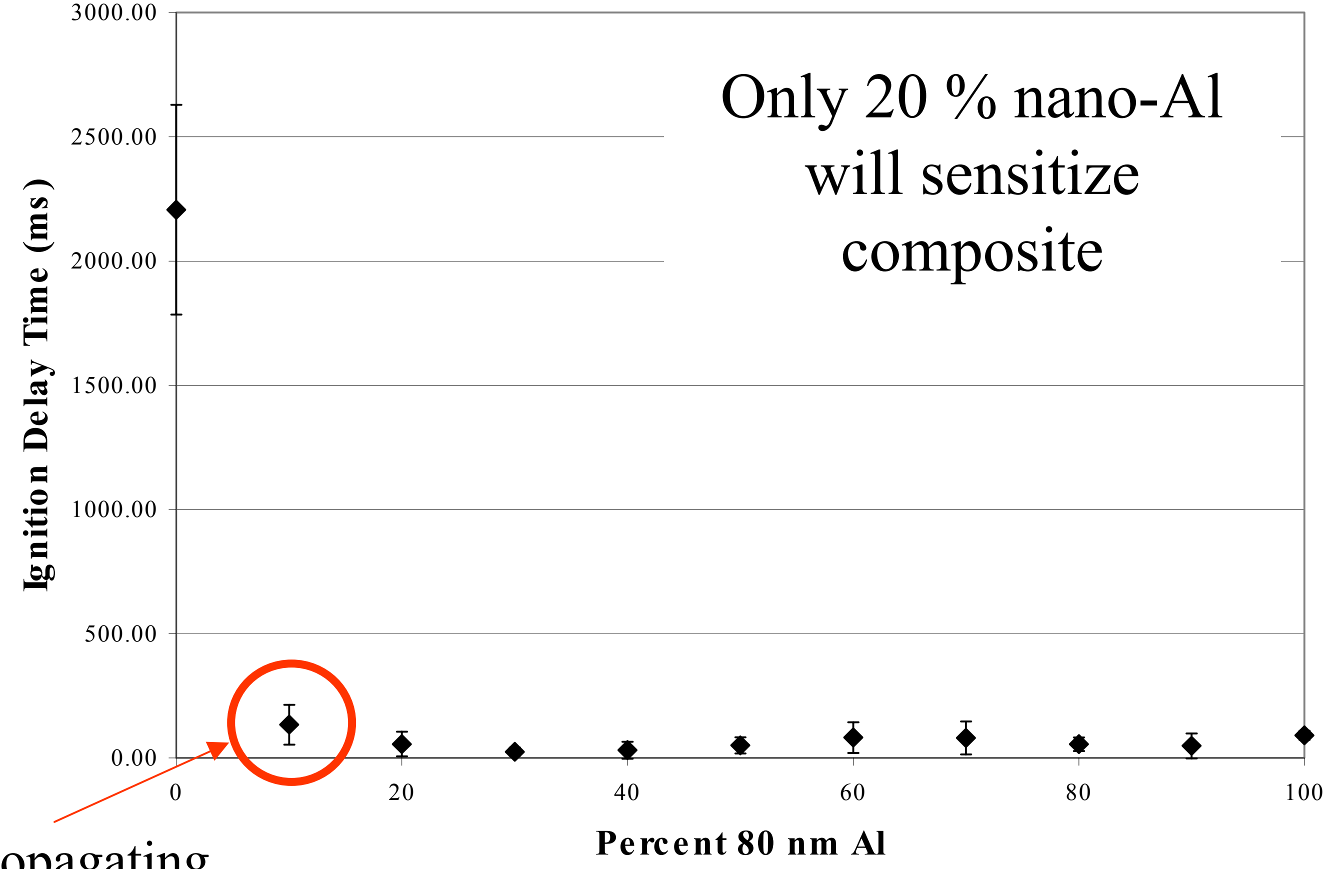
  (Popenko et al, Comb. Ex. Shock Waves Vol. 38 (2002))

  - Bound nitrogen content decreased dramatically when mixture is less than 20 % ultrafine Al
    - Incomplete combustion and sintering
- AP + bimodal Al

  (Dokhan, A. Price, E.W. Seitzman, J.M., Sigman, R.K., AIAA-2002-4173)

  - Significant increase in burn rate with only 20% addition of nano-Al.
    - Combustion takes place closer to the propellant surface
    - Increase in radiant and conductive heat feed back

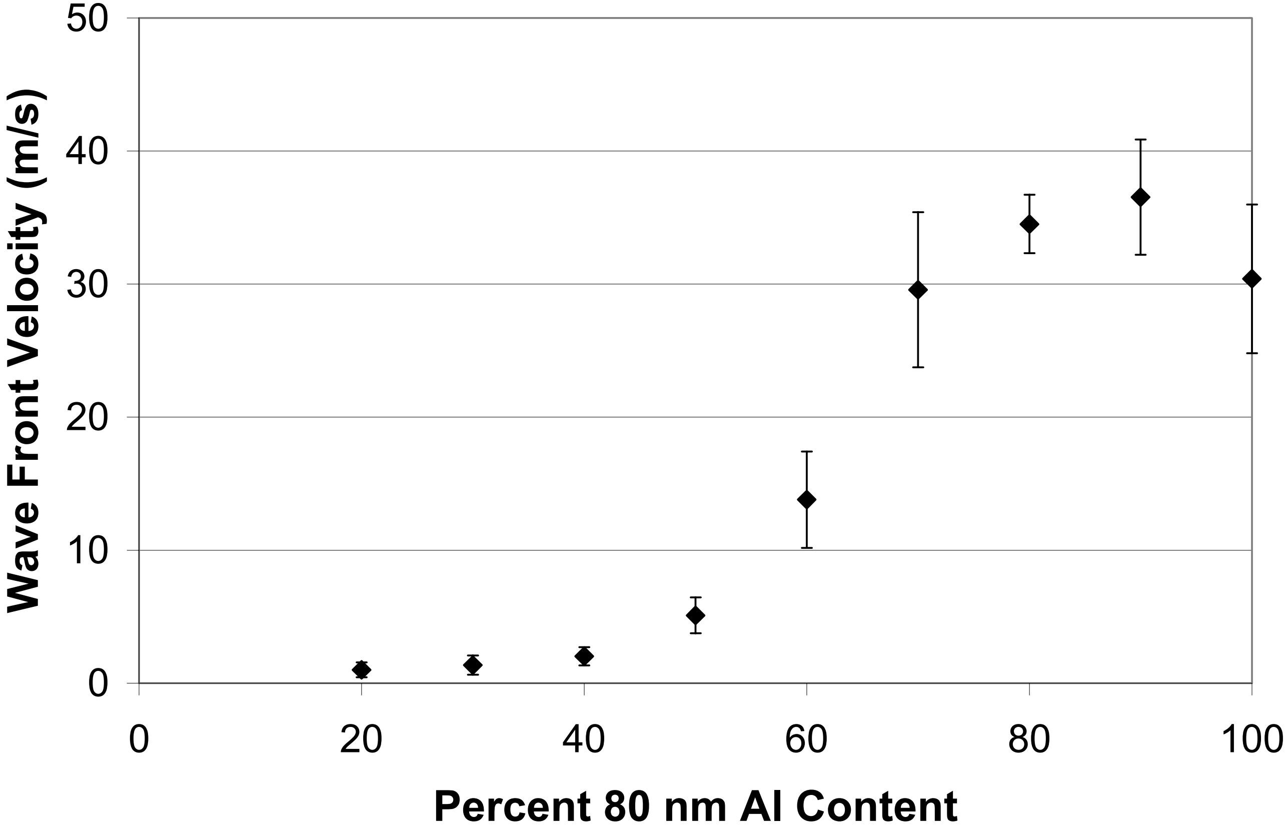
Bimodal: ignition behavior

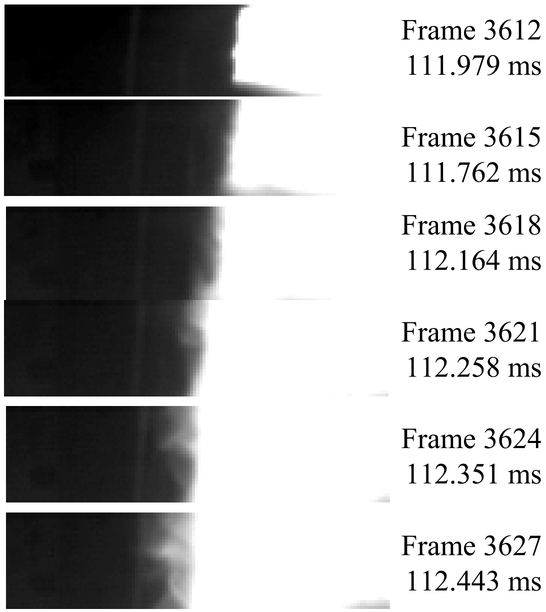


Only 20 % nano-Al will sensitize composite

Not Self-propagating

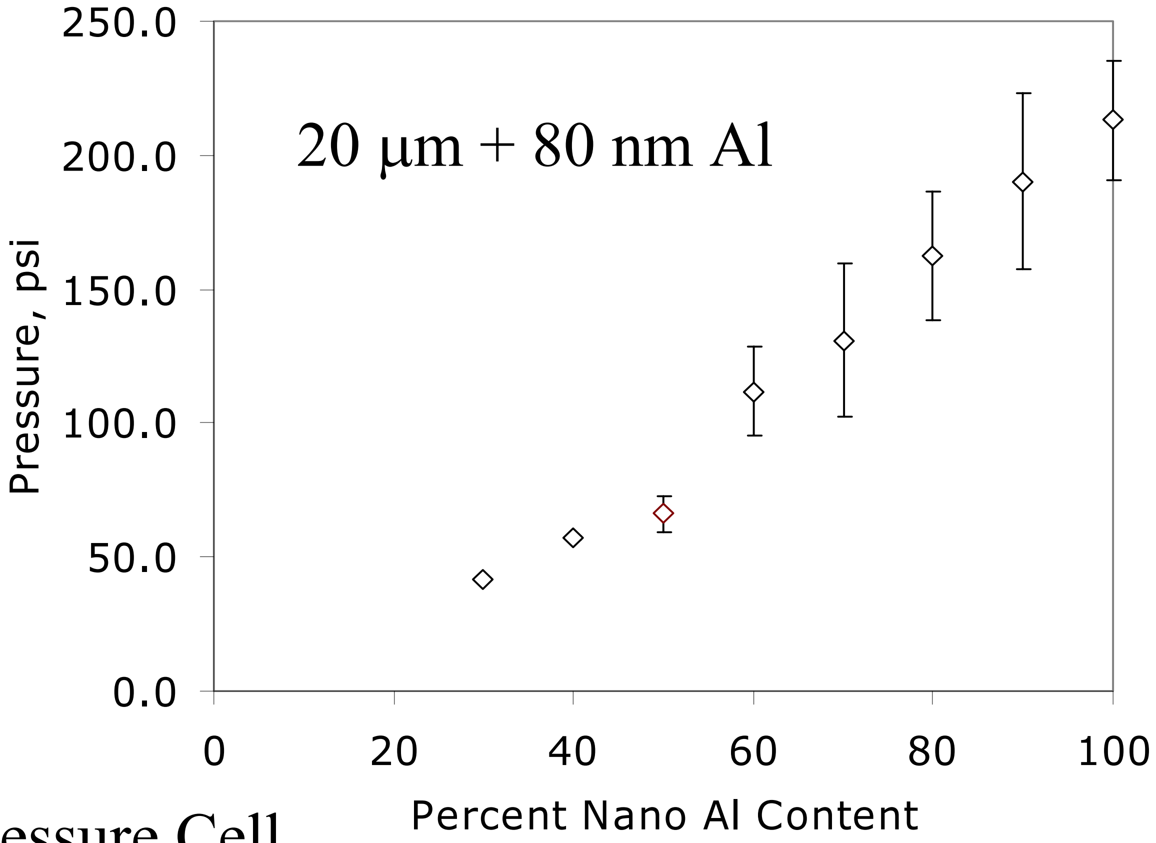
Bimodal: combustion wave speed in compact solids





Performance enhanced with 70 % nano-Al

Bimodal: normalized peak pressure in loose powders



LANL Pressure Cell

Linear increase in pressure implies incomplete reaction

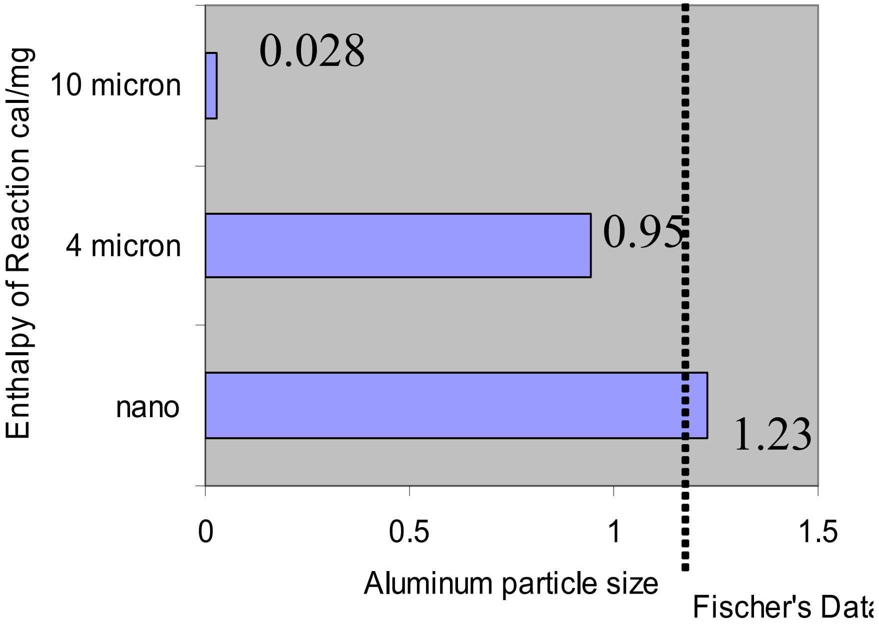
Bimodal: combustion wave speed

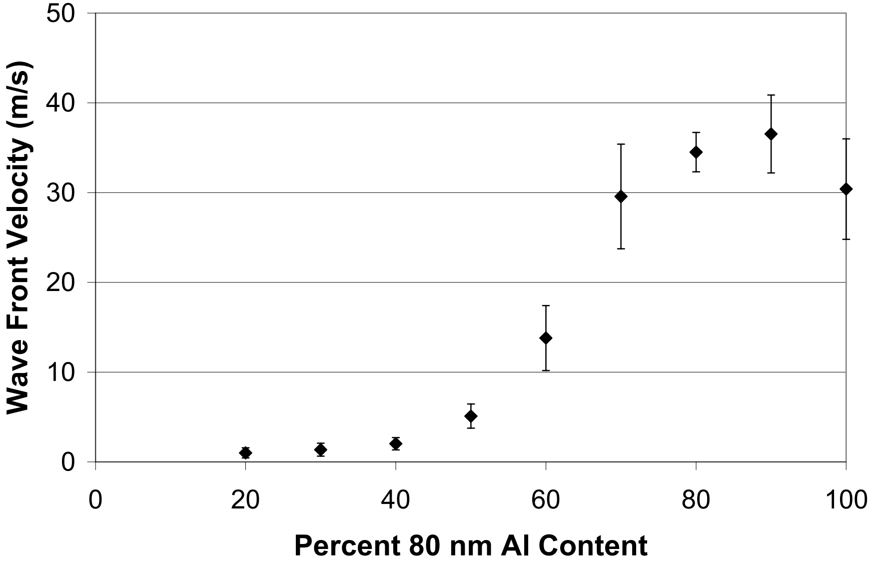
Convective burning: energy transfer in the burning zone driven by gas jets that penetrate into the pores of the energetic material.

Andreev number: $$\mathrm{An} = \frac{\rho_b U d_h c_p}{k_g}$$

ρ_b	is the bulk density of the composite	2200 kg/m^3
U	is the measured combustion wave speed	30m/s
d_h	is the hydraulic pore diameter	10^{-15} m
c_p	is the heat capacity of the composite	875 J/kgK
k_g	is the thermal conductivity of the gas	0.1 W/mK

Calorimetry $\mathrm{An} \sim 10^{-7}$





Conclusions

- Combustion performance depends strongly on equivalence ratio
  - Fuel rich appears optimal for reduce ignition delay time and increased combustion wave speed
- Nanocomposites are two orders of magnitude more ignition sensitive
  - Nanocomposites initiate reactions at much lower temperatures
  - This increased sensitivity leads to self propagation of solid-solid reactants which inhibits fast burn rates
- Role of bulk density is uniquely different in nano vs micron composites
- Particle size distribution will influence Al composites < 100 nm
  - Narrow distribution correlates to higher average velocity and smaller standard deviation
  - Bimodal particle mixtures may lead to incomplete reactions

Ludwig
Maximilians
Universität
München

High Tech
Campus LMU

Mechanistic studies concerning the hypergolic ignition between monomethylhydrazine (MMH) and dinitrogen tetroxide (NTO)

I. Frank,[a] T. M. Klapötke,[a] C. Nonnenberg [a] and H. Zewen [b]

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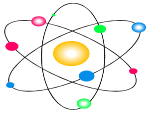
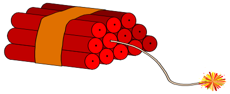
and
[b] EADS, Space Infrastructure, Ottobrunn, Germany

High Energy Density Materials: *Defense, Propulsion, Explosives & Fluorine*

research for science



and military



a past to build a future on

Hypergolicity

A hypergolic mixture ignites upon contact of the components without any external source of ignition (heat or flame).

The only fields in which this is a desirable event is in rocket fuels and in firebombs (incendiary devices).

One of the most common hypergolic systems for rocket fuels is a mixture of hydrazine and N_2O_4 (NTO); incendiary devices contain permanganate and glycol.

The hypergolic propellant oxidizer, nitrogen tetroxide (N_2O_4), and the fuels, hydrazine (N_2H_4) and monomethylhydrazine (MMH), are extremely reactive and toxic materials.

Theoretical performance of rocket propellant combinations

oxidizer	fuel	T_c / F	I_{opt} /
LOX	H_2	4964	389
	H_2 / Be (49/51)	4636	459
	CH_4	5900	310
	C_2H_6	6008	307
	B_2H_6	6312	342
	N_2H_4	5669	312
F_2	H_2	6672	412
	H_2 / Li (65/35)	3326	434
	MMH	7365	348
	N_2H_4	8062	365
OF_2	H_2	5992	410
FLOX (30/70)	H_2	5349	395
(88/12)	MMH	8049	360
N_2F_4	CH_4	6701	319
	N_2H_4	7617	335
ClF_5	MMH	6470	302
	N_2H_4	7041	313
ClF_3	MMH	6165	285
	N_2H_4	6602	294
N_2O_4	MMH	5652	289
	N_2H_4 / Be (80/20)	5500	327
MON-25 (25%	MMH	5707	290
	N_2H_4	5473	293
IRFNA (III-A)	UDMH	5205	272
IRFNA (IV HDA)	MMH	5347	280
	UDMH	5401	277
H_2O_2	N_2H_4	4804	287
	MMH	4924	285

Optimum expansion,
P_c = 1000 psia → P_e = 14.7 psia

IRFNA III-A: 83.4% HNO_3, 14% NO_2, 2% H_2O, 0.6% HF

IRFNA IV HDA: 54.3% HNO_3, 44% NO_2, 1% H_2O, 0.7% HF

I_{sp} [sec] = pounds of thrust / pounds of propellant / sec.

Ariane 512 Launch,
Kourou, French Guyana, 5th July 2002

DaimlerChrysler Aerospace

Space-Infrastructure

AESTUS
ARIANE 5 UPPER STAGE ENGINE

Injector
- 132 Coaxial/Slot Injection Elements

Combustion Chamber
- Regenerative Cooling with MMH 184 Milled Cooling Channels

Nozzle Extension
- Radiation Cooled
- Haynes 25
- Single Sheet

Propellants

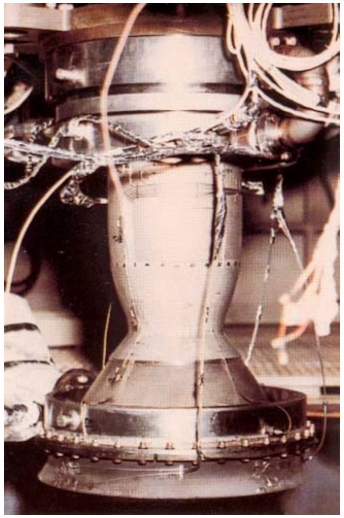
Nitrogentetroxide (N2O4)
Monomethylhydrazine (MMH)

Engine Main Data

● Vacuum Thrust	3 tons
● Vacuum Specific Impulse	324 sec
● Chamber Pressure	11 bar
● Nozzle Area Ratio	84
● Engine Mass	120kg
● Overall Length	2183 mm
● Re-ignition Capability	Multiple

Development Period
- 1988 - 1995

First Operational Flight
- Oct. 30, 1997; Ariane 5 Flight 502

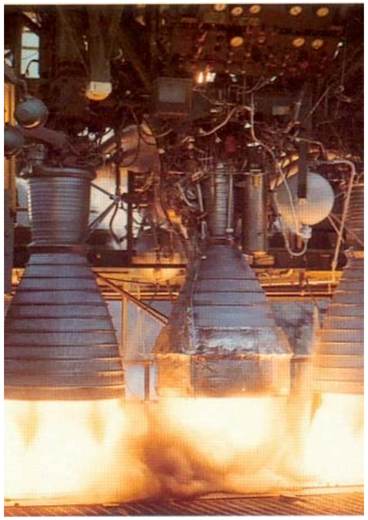


Orbit Engine
MMH/NTO = 1 : 1.65
I_{sp} = 313 s

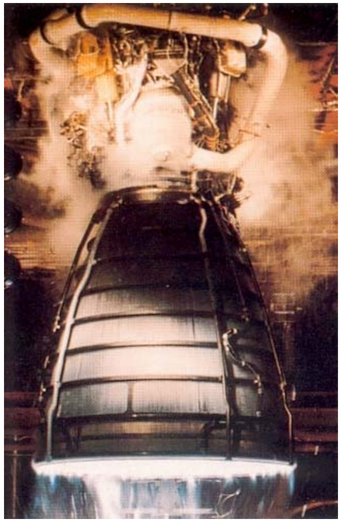
RS-44
LH2/LOX = 1 : 6
I_{sp} = 480 s

Space Engine
LH2/LOX = 1 : 6
I_{sp} = 473 s

RS-27, Delta
HC/LOX = 1 : 2
I_{sp} = 262 s



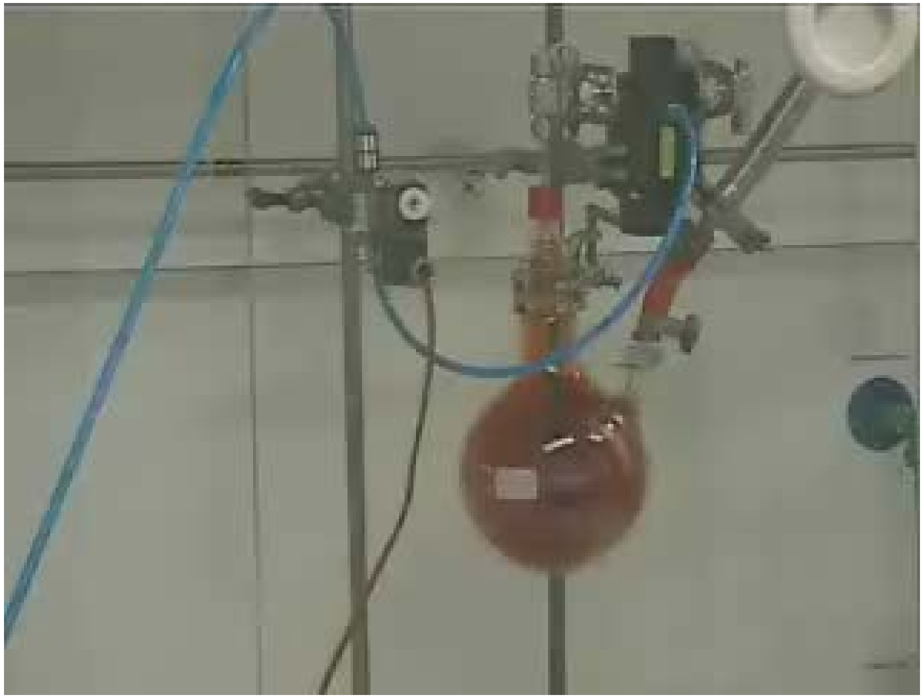
Atlas
HC/LOX = 1 : 2
I_{sp} = 250 s



Space Shuttle
LH2/LOX = 1 : 6
I_{sp} = 455 s

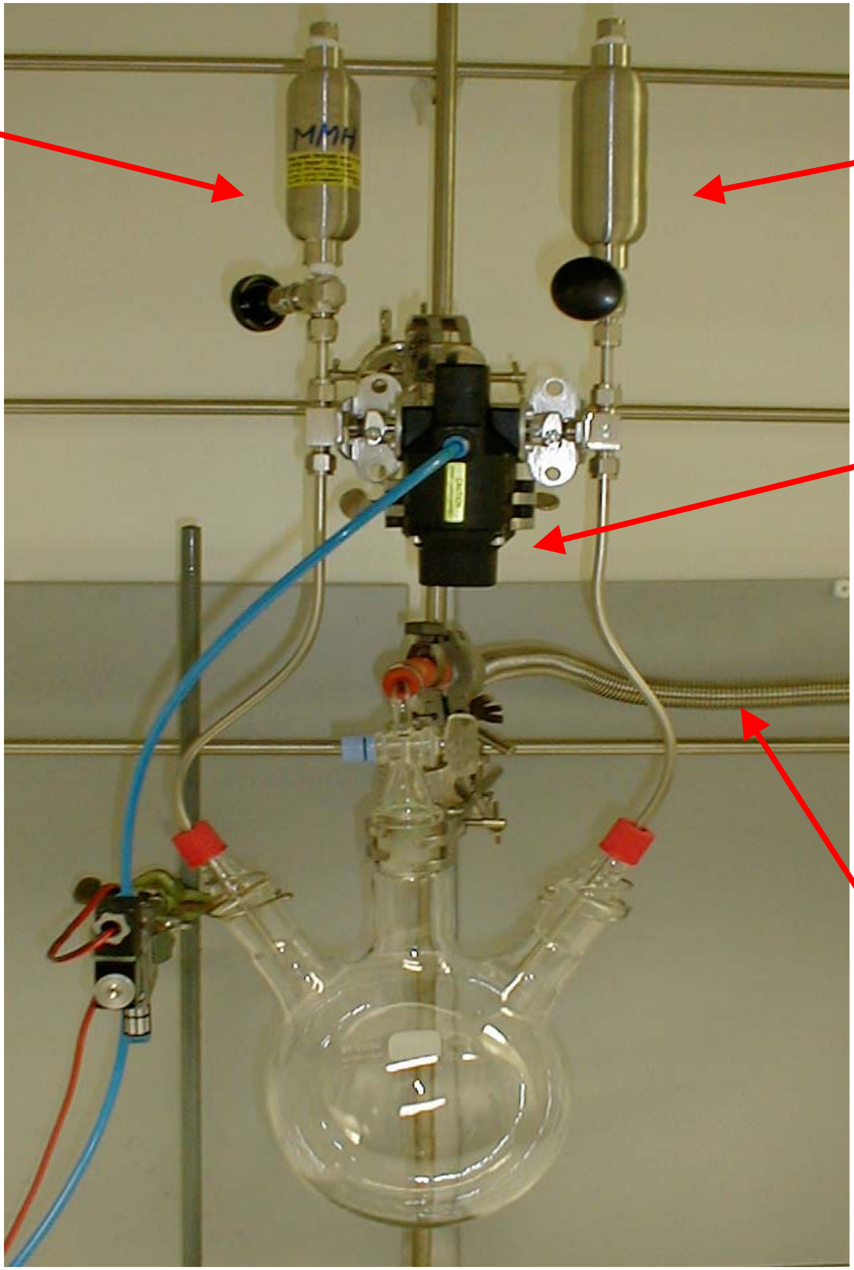
Reaction of NTO and MMH

Model of Ariane 5, Aestus upper stage combustion:



$N_2O_4 + (H_3C)NHNH_2 \longrightarrow 3\,N_2 + CO + 3\,H_2O$

Apparatus for the Reaction of MMH and NO_2



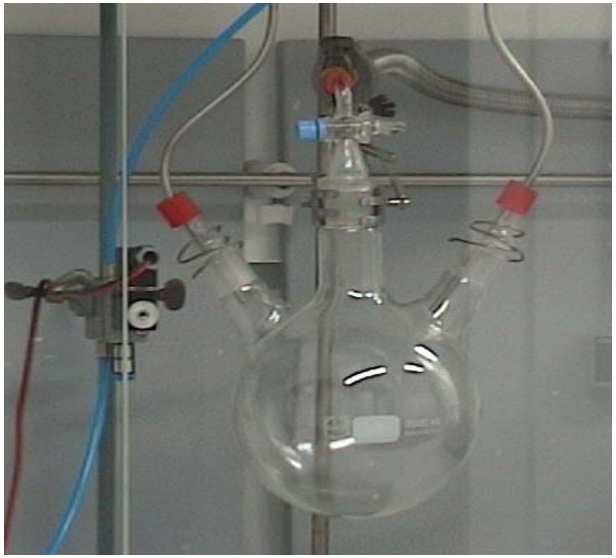
MMH

NO_2/ N_2O_4

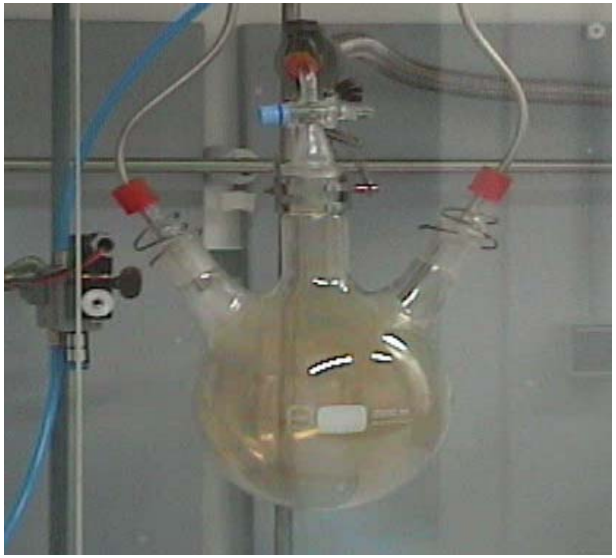
pneumatic valve

Dynamic vacuum; 10^{-3} torr

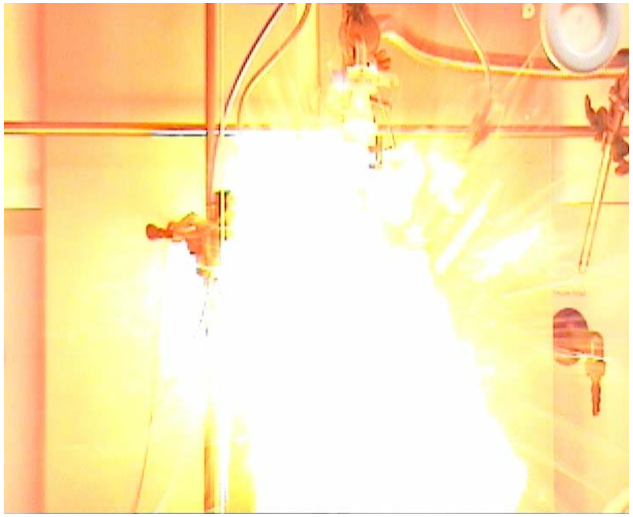
Reaction of MMH ((Me)HNNH$_2$) and NO_2



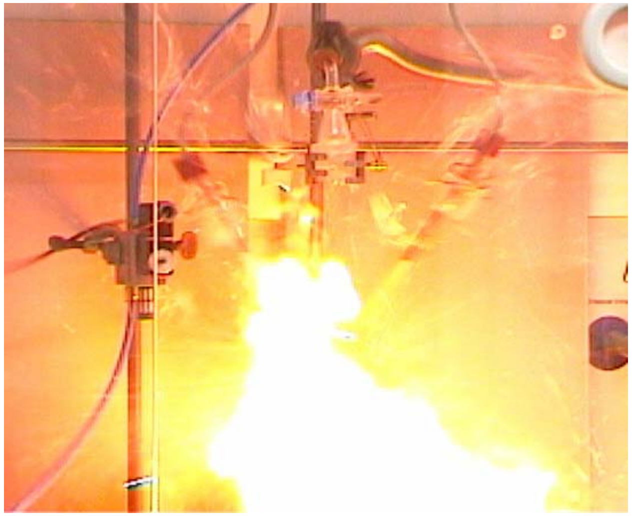
t = 0 (valves open)



t = 20 ms (valves open)



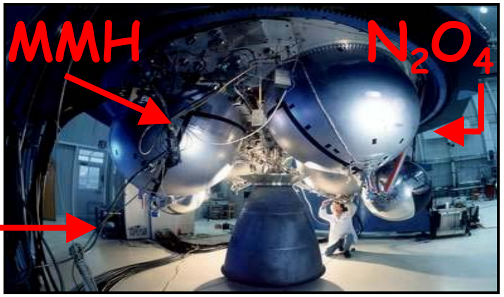
t = 40 ms (valves open)

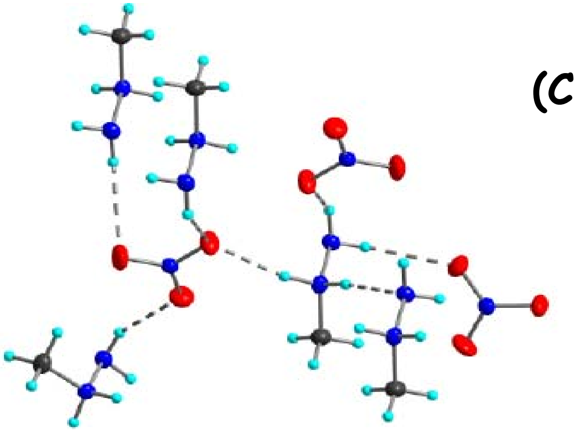


t = 60 ms (valves open)

Plume deposits from rocket engines

Upper stage Aestus engine





Methylhydrazinium nitrate

$(CH_3)HNNH_2 + HNO_3 \rightarrow [(CH_3)H_2NNH_2]^+[NO_3]^-$

monoclinic, $P2_1/c$,

$\rho = 1.54\ g\ cm^{-3}$

$a = 3.7794(4)$ Å, $b = 11.342(1)$ Å,
$c = 11.107(1)$ Å, $\beta = 99.09(1)°$,
$V = 470.15(9)$ Å^3, $Z = 4$

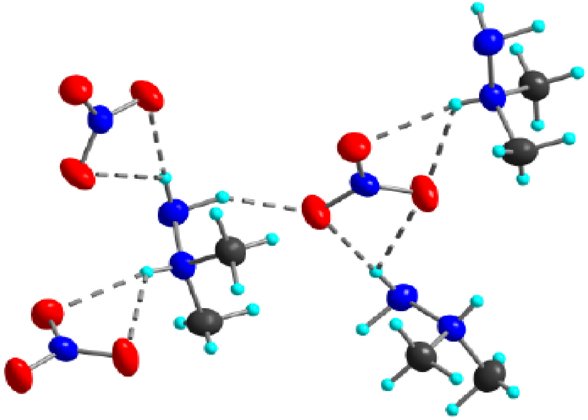
N,*N*-Dimethylhydrazinium nitrate

$[(CH_3)_2NHNH_2]^+[NO_3]^-$

orthorhombic, $Pna2_1$,

$\rho = 1.36\ g\ cm^{-3}$

$a = 14.0388(4)$ Å,
$b = 5.6493(1)$ Å,
$c = 7.6026(2)$ Å,
$V = 602.96(3)$ Å^3, $Z = 4$

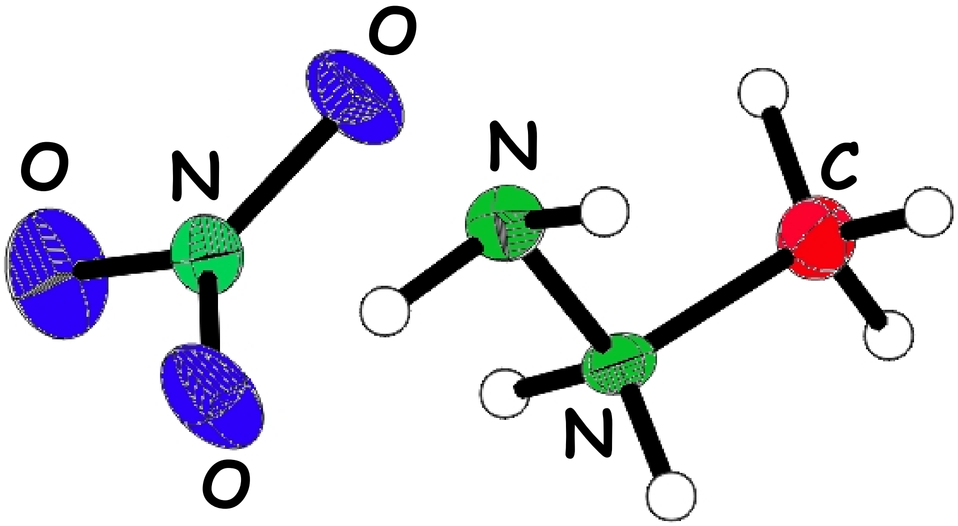


T. M. Klapötke et al. Z. Anorg. Allg. Chem., 627, 2001, 2011.

Methylhydrazinium nitrate

$[(CH_3)H_2N\text{-}NH_2]^+[NO_3]^-$

$$(CH_3)HNNH_2 \quad + \quad HNO_3 \quad \xrightarrow[-78°C]{CH_2Cl_2} \quad [(CH_3)H_2N\text{-}NH_2]^+[NO_3]^-$$



monoclinic, $P\,2_1/c$

a = 3.7794(4) Å, b = 11.342(1) Å, c = 11.107(1) Å

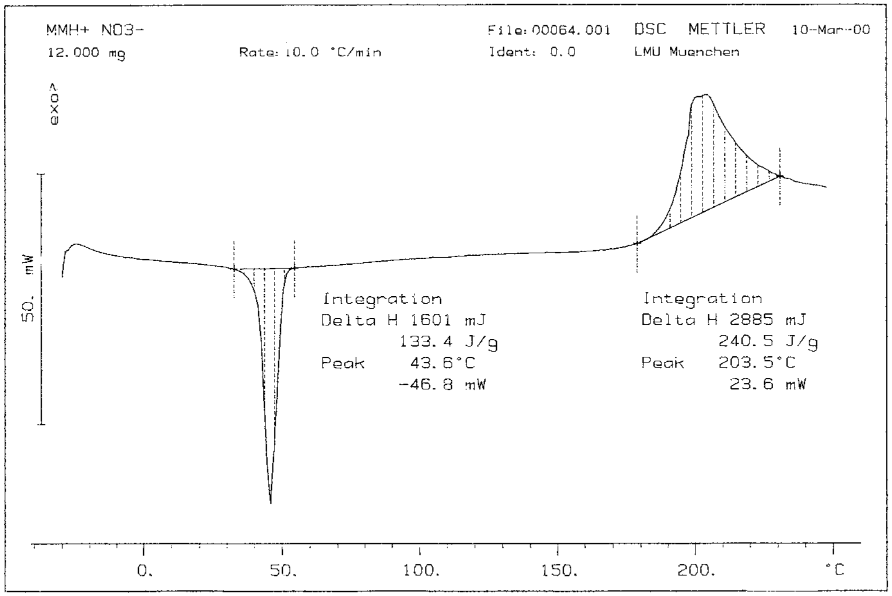
α = y = 90°, β = 99.09(1)°

V = 470.15(9) Å^3, Z = 4

ρ = 1.54 g cm^{-3}

Differential Scanning Calorimetry (DSC) MMH nitrate

- two phase transitions in the DSC diagram
- one endothermic at 43.6°C and one exothermic at 203.5°C
- 43.6°C → melting point
- 203.5°C → decomposition



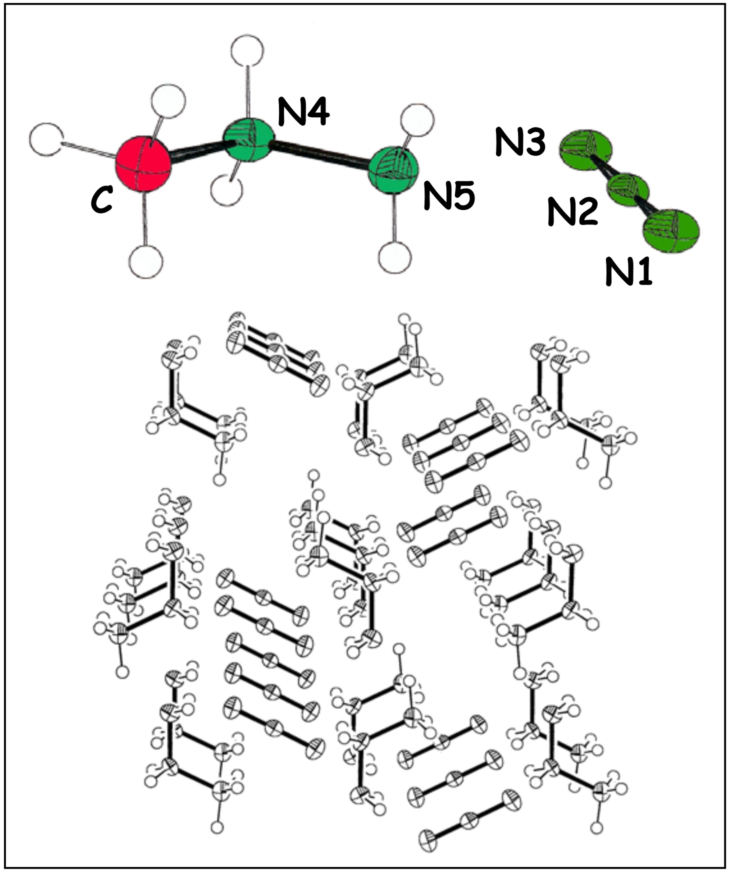
mp:	42 °C
^{1}H NMR ([D6]DMSO):	δ = 1.65 (s, 3 H, CH_3), 6.52 (s, 4 H, NH)
^{13}C NMR ([D6]DMSO):	δ = 37.6 (CH_3)
^{14}N NMR ([D6]DMSO):	δ = 1 ($\underline{N}O_3$), -360 ($CH_3\underline{N}H_2\underline{N}H_2$).
elemental analysis:	calcd.: 11.01 % C, 6.47 % H, 38.52 % N
	found: 10.95 % C, 6.32 % H, 38.19 % N

Firing test of $(H_3C)NH_2NH_2^+NO_3^-$

Methylhydrazinium azide

$[(CH_3)H_2N\text{-}NH_2]^+[N_3]^-$

$$(CH_3)HNNH_2 + HN_3 \xrightarrow{Et_2O} [(CH_3)H_2N\text{-}NH_2]^+[N_3]^-$$



orthorhombic, space group *Pnma*,

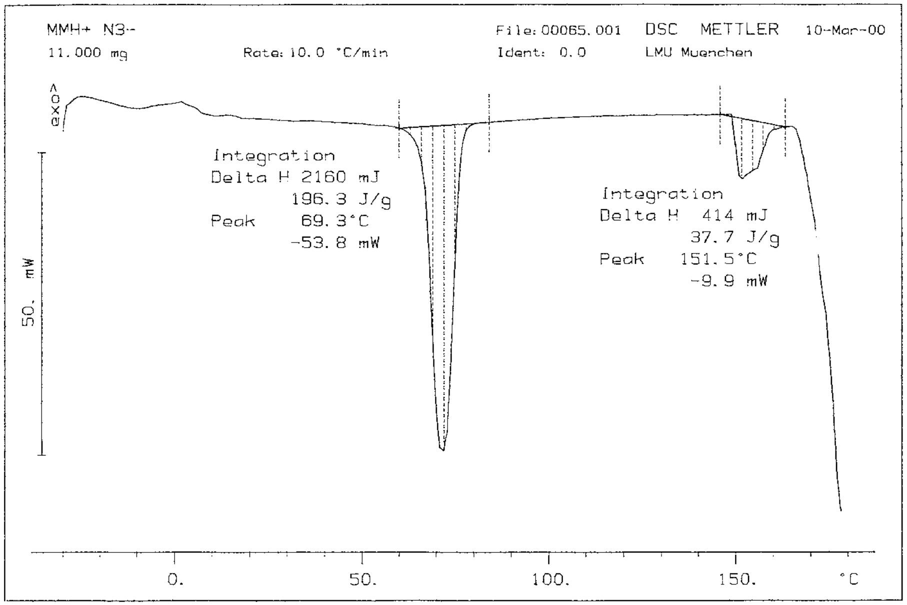
a = 9.962(1), *b* = 5.1316(5), *c* = 9.2280(9) Å, *α* = *b* = *γ* = 90°, ρ = 1.255 g cm^{-3}

Differential Scanning Calorimetry (DSC) MMH azide

* two endothermic phase transitions in the DSC diagram

69.3°C → melting point

151.5° → (boiling) decomposition point.



mp: 68°C

^1H NMR ([D6]DMSO): δ = 2.50 (s, 3 H, $C\underline{H}_3$), 6.89 (s, 4 H,N$\underline{H}$).

^{13}C NMR ([D6]DMSO): δ = 37.6 ($\underline{C}H_3$).

^{14}N NMR ([D6]DMSO): δ = -134, -278, -353 ($Me\underline{N}H_2\underline{N}H_2$)

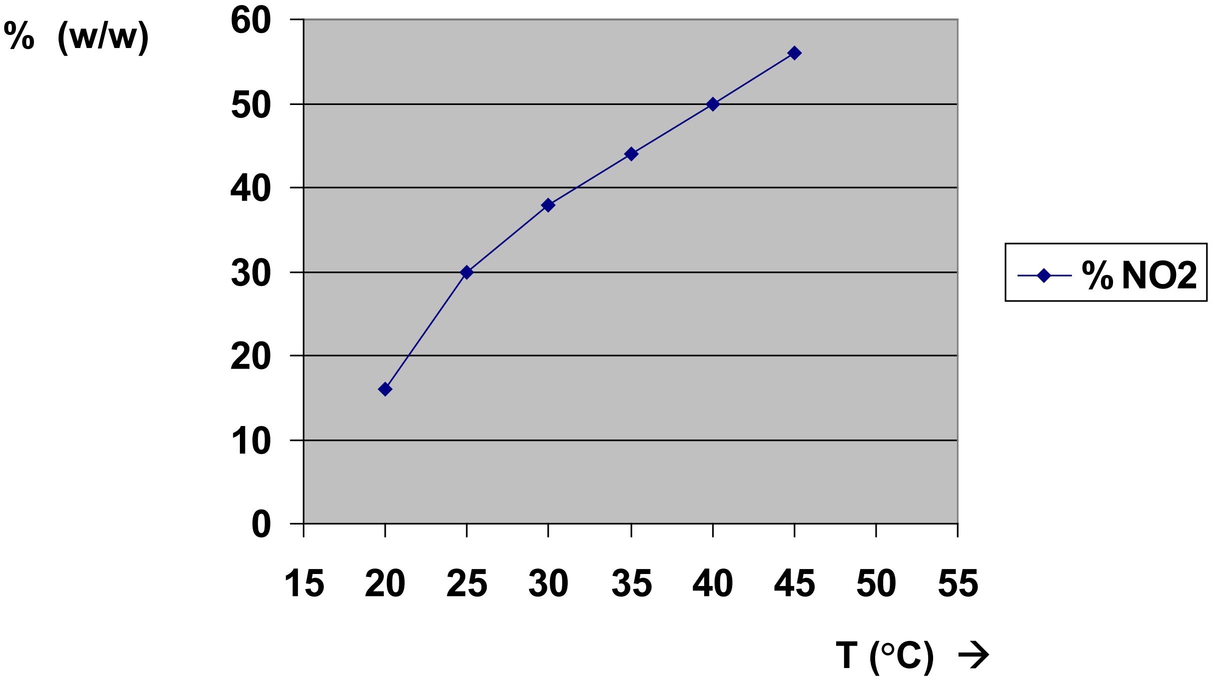
^{15}N NMR (D_2O): δ = -132 ($\underline{N}N\underline{N}$), -280 ($N\underline{N}N$), -358 ($H_2\underline{NN}H_2CH_3$).

elemental analysis: calcd.: 13.48% C, 7.92% H, 78.60% N.

found: 13.23% C, 7.83% H, 78.55% N.

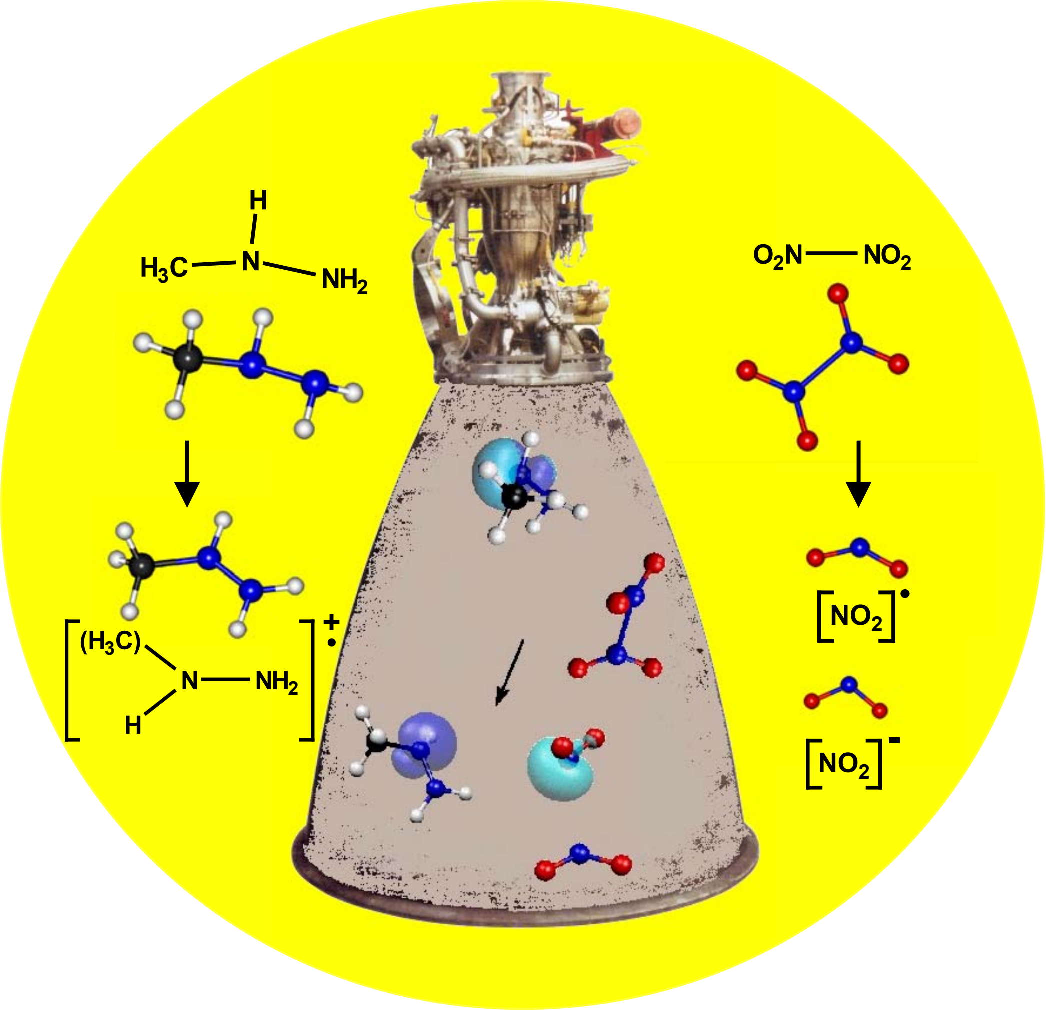
Temperature dependence of the N_2O_4 (NTO) NO_2 equilibrium

$$N_2O_4 \rightarrow 2\,NO_2$$



Composition of N_2O_4/NO_2 at a total vapor pressure of ca. 0.35 atm in percent (weight by weight).

Cold Pre-Ignition Reaction between MMH and NTO



Frank, Klapötke et al., Angew. Chemie Intl. Ed., September 2004.

Molecular Dynamic (MD) Study

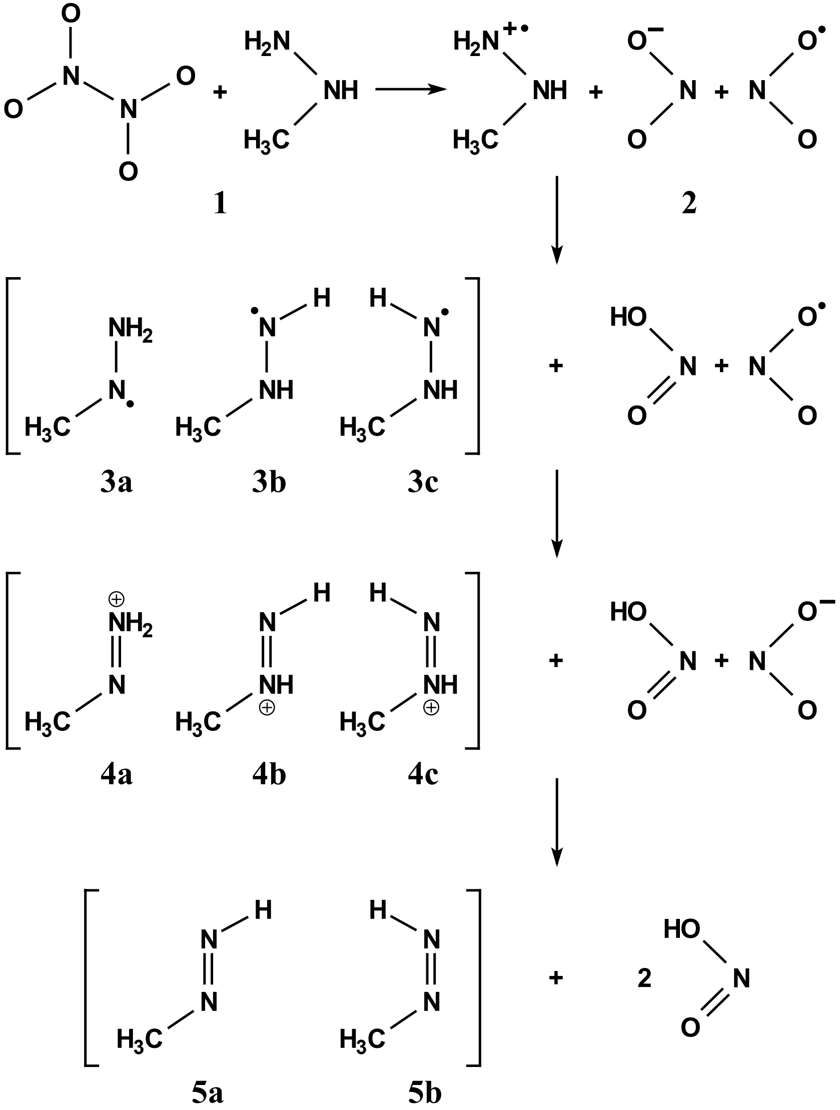
Method	Car-Parrinello MD (first principles) simulation
Time scale	femto seconds to pico seconds
Level of theory	DFT, BLYP
System	MMH/NTO, ratio = 1:1, density = 0.9 g cm^{-3}
Temperature	300 K

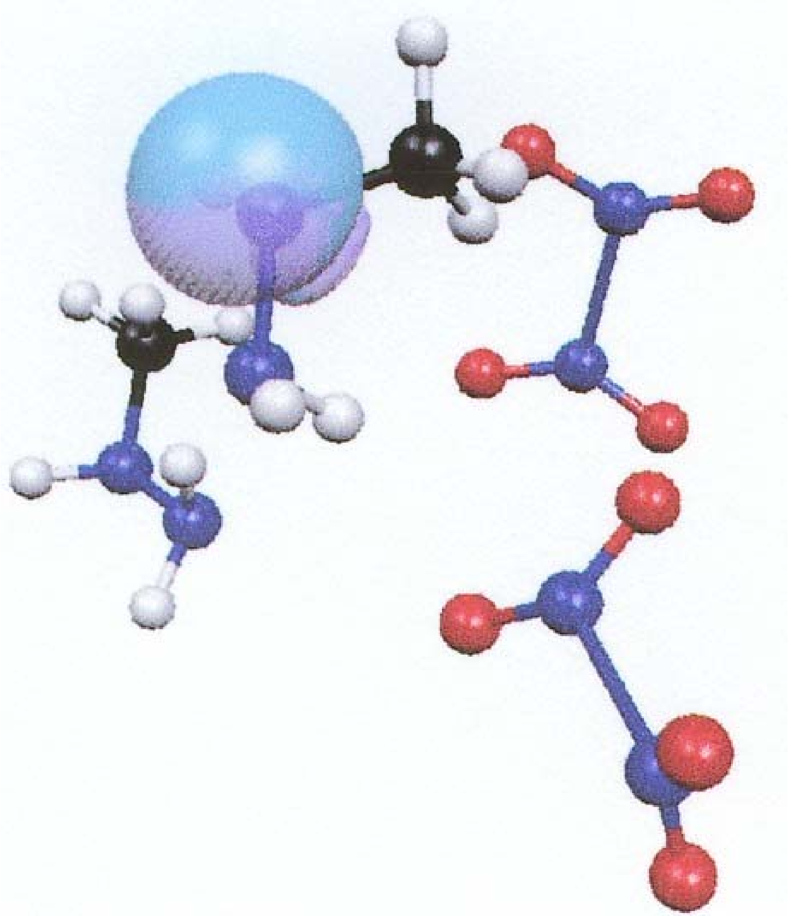
Car-Parinello Molecular Dynamics

- **The problem:** Nuclear and electronic motions have widely differing time scales.
- Classical approaches track atomic motions and uses a macroscopic force field to include electronic effects. Quantum approaches track electronic effects in a field of fixed nuclear positions. Adding an iterative method, one can include the motion of the nuclear positions.
- Can these be combined? Should they be combined?
- One method to combine the electronic and nuclear motions is Quantum Molecular Dynamics first proposed by Car and Parinello.

  The approach is to treat the electronic degrees of freedom in a manner similar to the particle coordinates, by assigning a fictitious mass to the functions describing the electronic degrees of freedom. This is usually a Molecular Orbital derived from traditional Hartree-Fock (Wave Function Functionals) using both the usual molecular Hamiltonian, a semi-empirical Hamiltonian, or a Kohn-Sham Orbital derived from Density Functional Theory (DFT) formalism. This approach is also referred to as "Dynamic Simulated Annealing" This is because rather than using a Monte Carlo approach to describe the changing electronic state, Car and Parinello used a molecular dynamics approach to implement simulated annealing. The MD equations of motion are used to move around configuration space. In this case, the degrees of freedom of configuration space are the coordinates of the atomic centers and the electronic degrees of freedom.

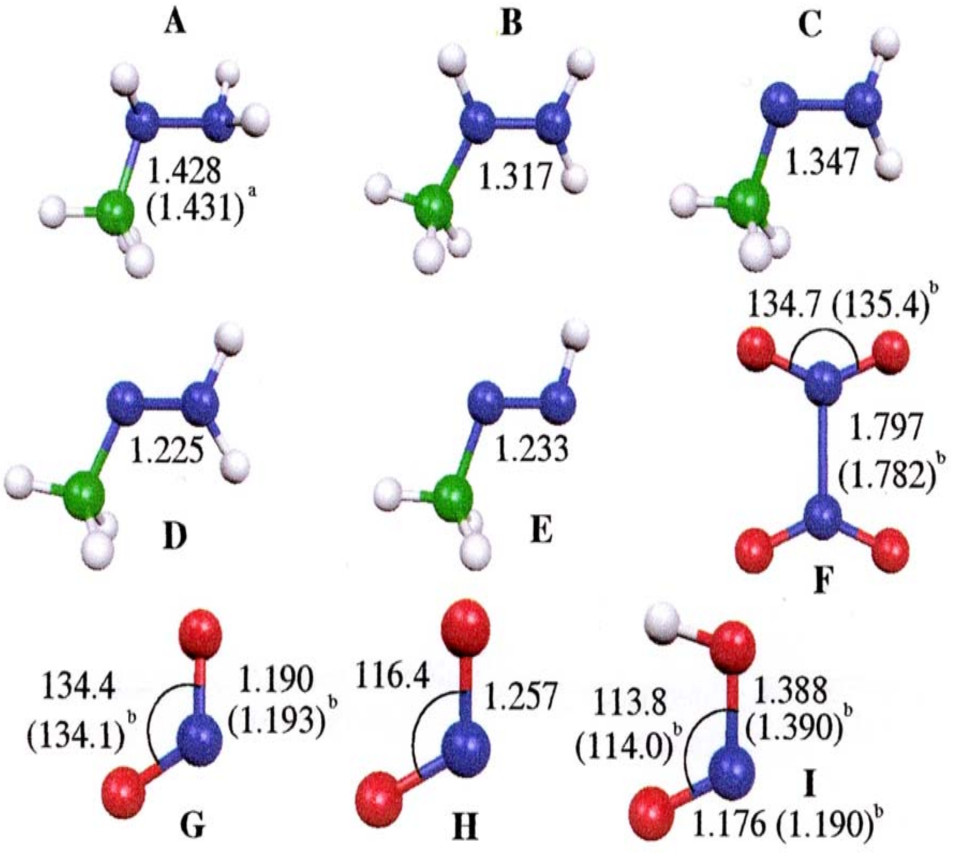
Redox Reaction between MMH and NTO to Yield Methyldiazene (CPMD Simulation)





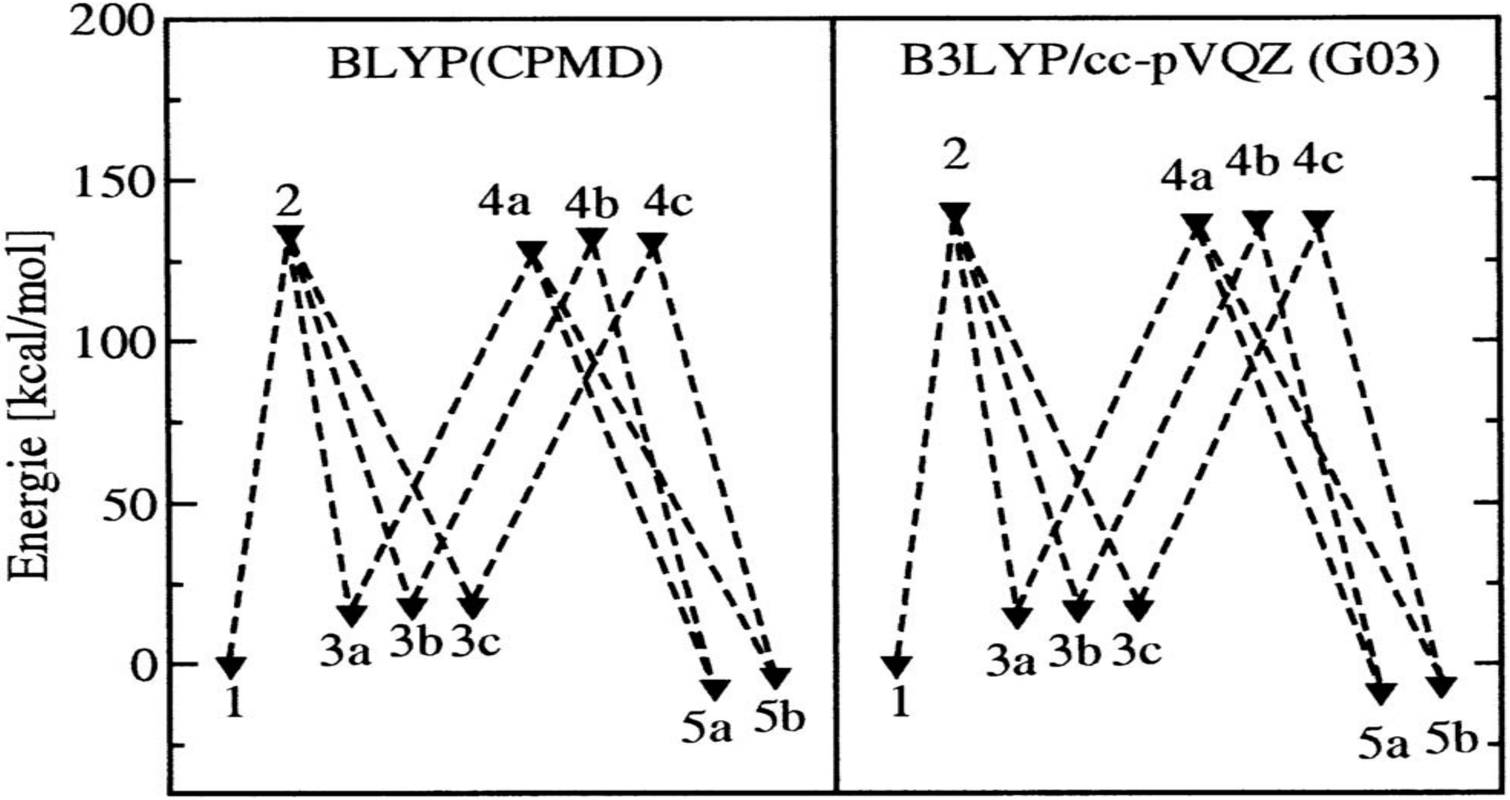
highly reactive MMH/NTO intermediate

B3LYP/cc-pvQZ calculated geometries

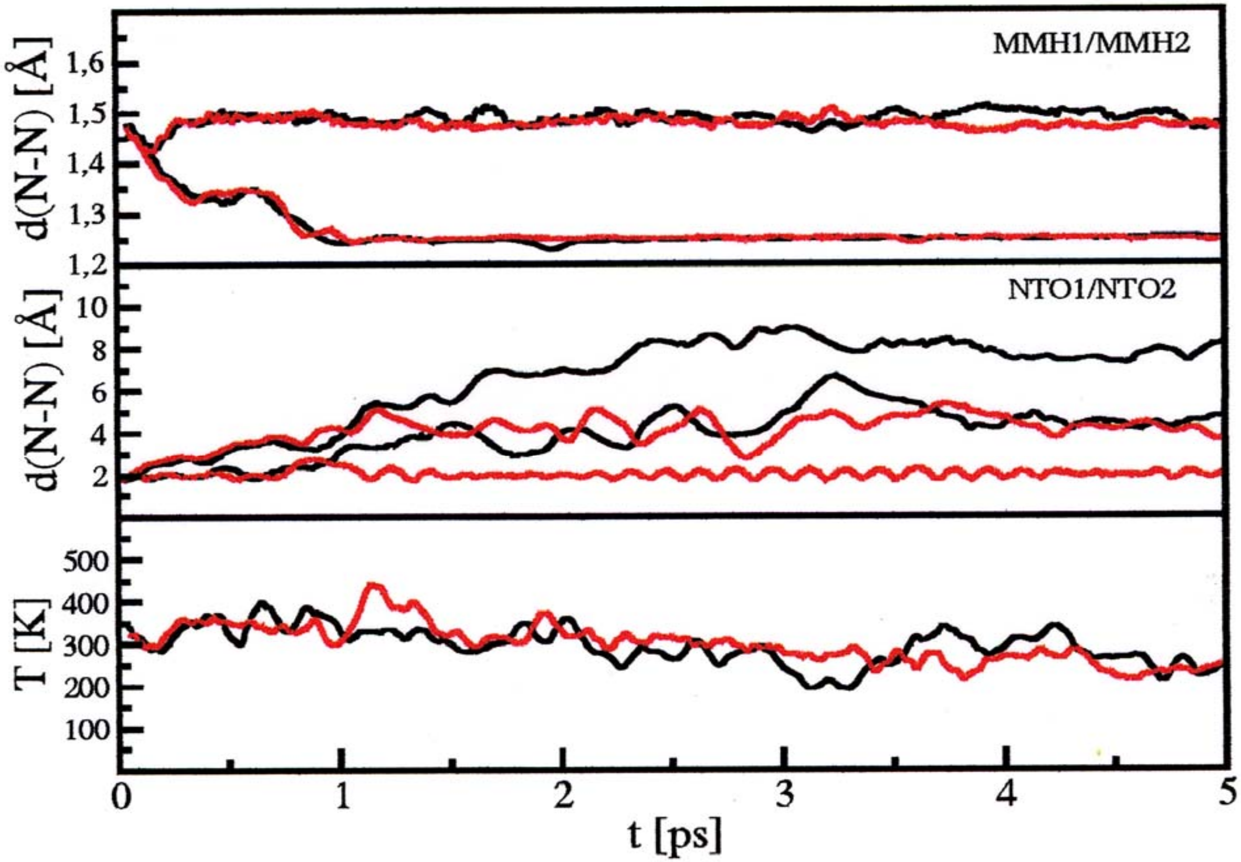


A: MMH
B: MMH, radical cation
C: Methylhydrazyle radical
D: protonated methyldiazene
E: trans-methyldiazene
F: NTO
G: NO_2 radical
H: NO_2^- anion
I: HNO_2

Relative Energies of the Redox Reaction: MMH → Methyldiazene

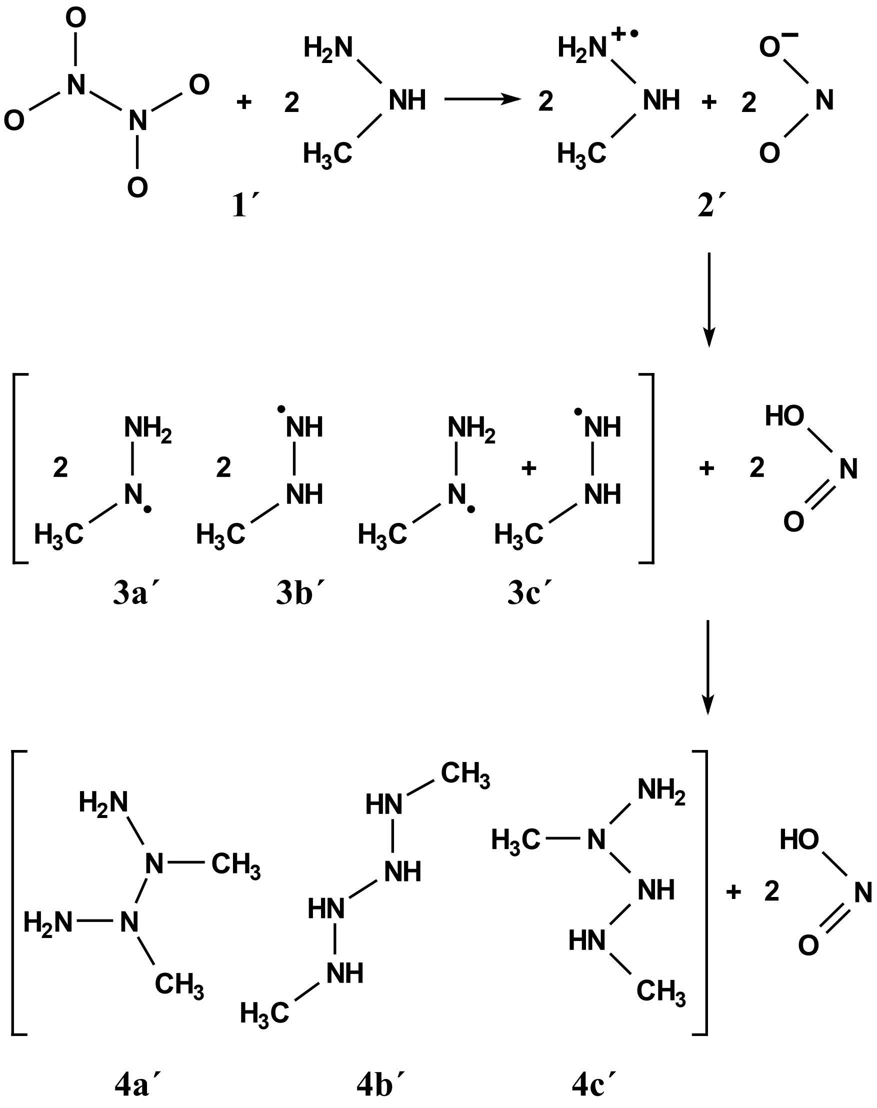


Simulation of a 1:1 Mixture of MMH/NTO (density 0.9 g cm^{-3})

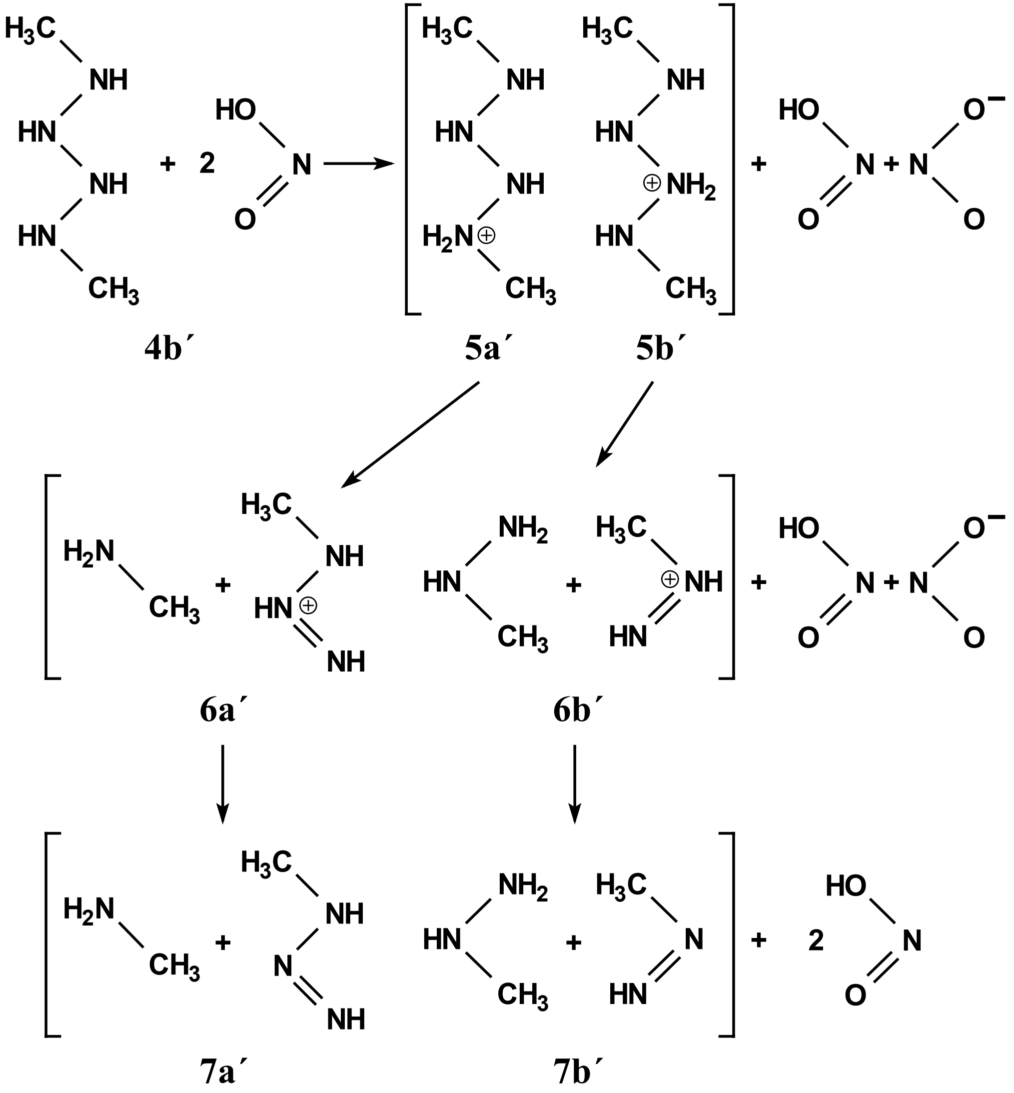


Upper box:
d(N-N) in MMH [A]
Center box:
d(N-N) in NTO [A]
Bottom box:
temperature, T [K]

Formation of Dimethyltetrazana Isomers (from MMH excess)



Reaction Scheme for the Degradation of Dimethyltetrazane due to Acid-Base Reactions



Conclusions from the CPMD/BLYP Study

- The (cold) pre-ignition reaction between MMH and NTO can be explained by the oxidation of MMH to methyldiazene (monomethyldiimine, $CH_3N=NH$), this reaction occurs without significant heat release.
- Especially at low temperatures and with MMH excess the formation of dimethyltetrazane due to the recombination of two methylhydrazyle radicals is likely.

  Subsequent decomposition of the highly energetic tetrazame may cause a (very) exothermic reaction.

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C. Nowak
G. Spieß

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Univ. Maryland, USA: Theory

Dr. J. Li
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VB Theory

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EADS, Ottobrunn: Propulsion

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WIWEB, Erding: HEDM

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Univ. Glasgow, Scotland: Catalysis

Research Group of Prof. Dr. Thomas M. Klapötke
Professor of Inorganic Chemistry
http://www.chemie.uni-muenchen.de/ac/klapoetke/index.html

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High Energy Density Materials: *Defense, Propulsion, Explosives & Fluorine*

research for science **and military**

a past to build a future on

WIWEB **Wehrwissenschaftliches Institut für Werk-, Explosiv- und Betriebsstoffe**

***I am one of those who think like Nobel,
that humanity will draw more good
than evil from new discoveries.***

Marie Curie

***We will not waver; we will not tire; we will not falter;
and we will not fail. Peace and freedom will prevail.***
George W. Bush, 2001

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Synthesis, Structure, Molecular Orbital and Valence Bond Calculations and Decomposition Mechanism for Tetrazole Azide, CHN_7

Thomas M. Klapötke,[a] Anton Hammerl [a] and Gerhard Holl [b]

[a] Chair of Inorganic Chemistry,
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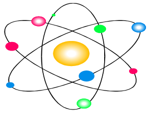
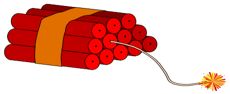
Fuels and Lubricants, Erding, Germany

High Energy Density Materials: *Defense, Propulsion, Explosives & Fluorine*

research for science



and military



a past to build a future on

Today's …

… explosives

melt-casting	TNT
energetic fillers	RDX, HMX
energetic binders	NC, GAP (glycidyl azide polymer, MW=2000) (e.g. RDX:GAP = 80:20)
energetic plasticizers	NG, other nitrate esters

… propellants

solid boosters	AP / Al + binders
main stage (cryogenic)	H_2 / O_2
upper stage	N_2H_4, MMH, UDMH / NTO; HC / NTO, HNO_3, H_2O_2

… primary explosives

lead azide, $Pb(N_3)_2$

… are (often) the solutions to yesterdays problems

Future weapons should be:

- smaller
- lighter
- more lethal
- more reliable
- fuel efficient
- more survivable

Survivability increases with:

- low observable plumes
- ballistic protection
- long-range
- deep-targeting
- early attack
- first round kill

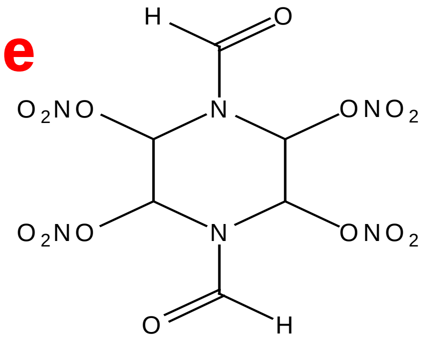
Goals for the Preparation of Novel High Energy Density Materials (HEDM)

- ✓ ρ = high (density)
- ✓ T dec. = high, >> T mpt.; m.pts. = high (>100°C)
- ✓ no heavy metals or halogens
- ✓ nitrogen rich: compounds containing H, C, N, O ideal if they form non-toxic combustion products
- ✓ undetectable with radar
- ✓ smokeless combustion, minimum signature
- ✓ not too toxic (EM's and products), environmentally benign
- ✓ high energy release
- ✓ high yield, easy, large scale syntheses
- ✓ cheap starting materials
- ✓ high stability: thermal, friction, shock
- ✓ good ageing properties (longevity)
- ✓ better "energy coupling with the target" (= f(r))
- ✓ better formulations (ρ, eng. binders and plasticizers etc.)

Strategies for the Synthesis of New (Environmentally Compatible) Energetic Materials

- **Oxidation of molecule back-bone**

  (*e. g.* addition of nitro or nitrato (NO_2, NO_3) groups to ring)

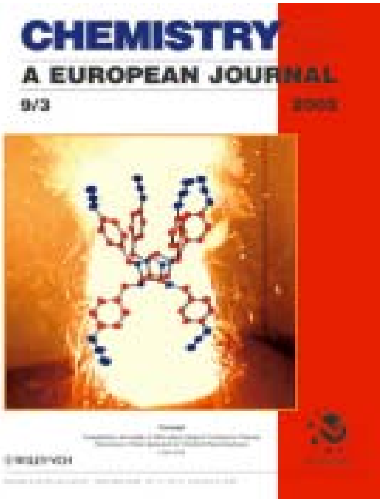


Klapötke, T. M. et al., Prop. Exp. Pyro, 2003

- **Cage strain**

  (no cage strain in explosion products)

Klapötke, T. M. et al., Chem. Eur. J., 2003


CHEMISTRY
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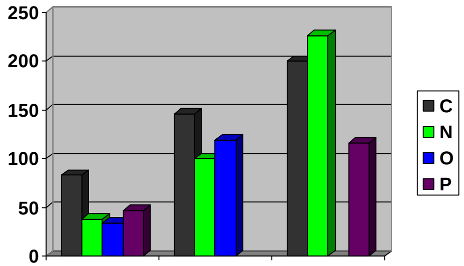
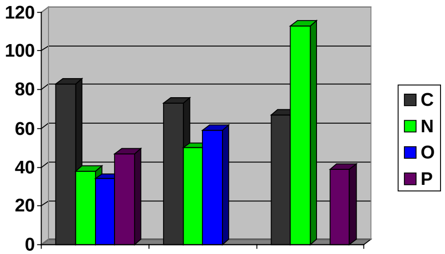
9/3 2003

- **Highly Endothermic N Rich Compounds**

  (N—N bonds present form N≡N bonds after explosion)



X-X, X=X, X≡X bond energies



X-X X=X X≡X
formal average bond energies per 2-electron bond

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T.M. Klapötke* et al. (Germany)

2

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N. Wingborg,* C. Eldsäter (Sweden)

3

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P. Brousseau,* C.J. Anderson (Canada)

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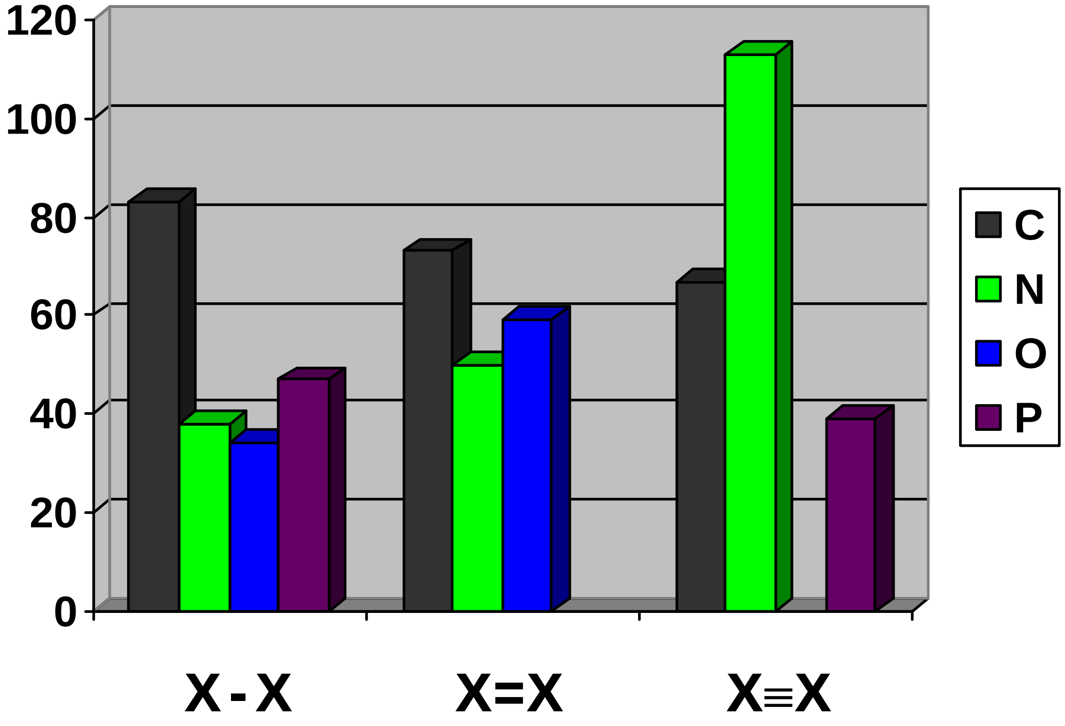
Highly Endothermic Nitrogen Rich Compounds

(N—N bonds present form N≡N bonds after explosion)



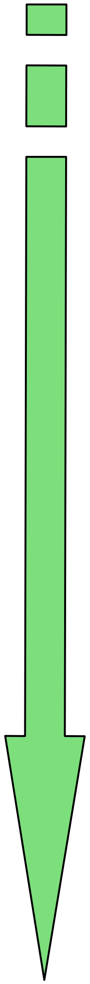
formal average bond energies per 2-electron bond

Benefits of All-Nitrogen (& N-Rich) Compounds

- ⇨ only gaseous products
- ⇨ large heats of formation (ΔH°_f)
- ⇨ high propulsive / explosive power
- ⇨ high specific impulse (200% > N_2H_4)
- ⇨ very high flame temperature
  (up to 7500 K, adiabatic flame)
- ⇨ smokeless combustion
- ⇨ minimum signature
- ⇨ reduce erosion, reduce C content (low CO)
  (for gun propellants)

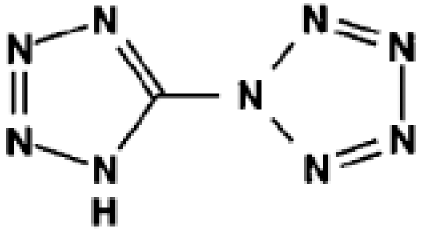
Nitrogen-Content of Some Nitrogen-Rich Materials

$[NH_4][NO_3]$	ammonium nitrate	35.0 %
$[NO_3][CH_5N_6]$	$[HDAT][NO_3]$	60.1 %
CH_3NH-NH_2	methylhydrazine	60.9 %
H_2N-CN_4H	aminotetrazole	82.4 %
CH_4H_6	DAT	84.0 %
$[N_2H_5]_2[C_2N_{10}]$	hydrazinium azotetrazolate	85.2 %
N_2H_4	hydrazine	87.5 %
CHN_7	tetrazole azide	88.3 %
$[N_2H_5][N_3].N_2H_4$	hydrazinium azide hydrazinate	91.5 %
$[NH_4][N_3]$	ammonium azide	93.3 %
$[N_2H_5][N_3]$	hydrazinium azide	93.3 %
HN_3	hydrazoic acid	97.7 %
N_2	dinitrogen	100 %

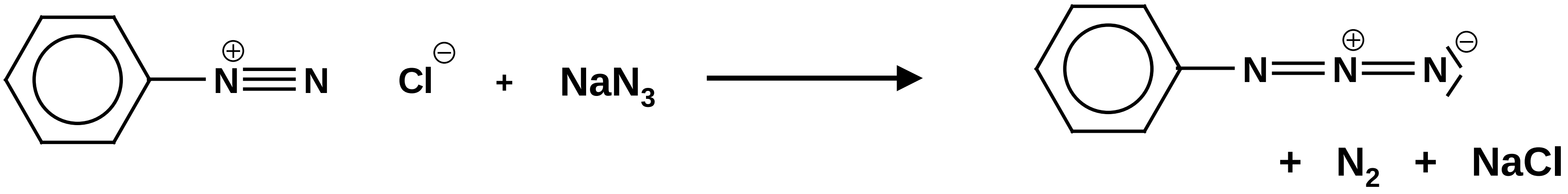


Nitrogen content

Compounds with a Nitrogen Content > 90 % (macroscopic quantities)

Compound	N-content	
N_2	100 %	
$N_5^+B(N_3)_4^-$	95.7 %	Christe et al. 2004
$N_2H_5^+N_3^-$	93.3 %	Curtius, 1887
$NH_4^+N_3^-$	93.3 %	Curtius, 1891
$N_2H_5^+N_3^- \bullet N_2H_4$	91.5 %	Klapötke et al., 2001
$Li^+B(N_3)_4^-$	90.4 %	Klapötke et al., 2001
	90.6 %	Klapötke et al., 2002 (not isolated)

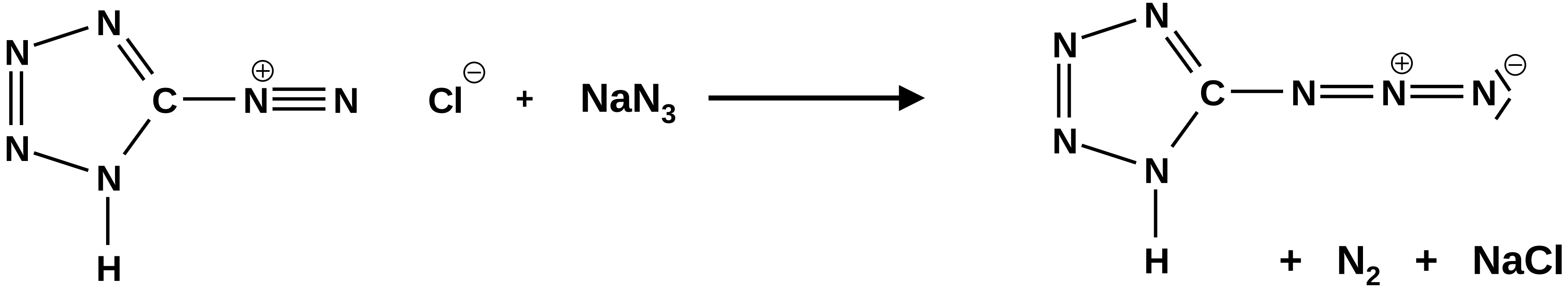
Synthesis of Pentazole Intermediates



Aryldiazonium chloride

Aryl azide

Huisgen, Ugi et al., *Angew. Chem.*, 1956, 68, 753.

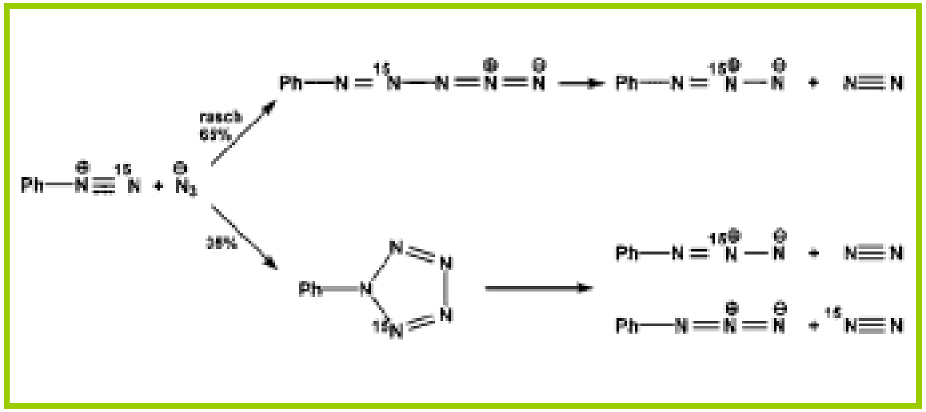


Tetrazolediazonium chloride

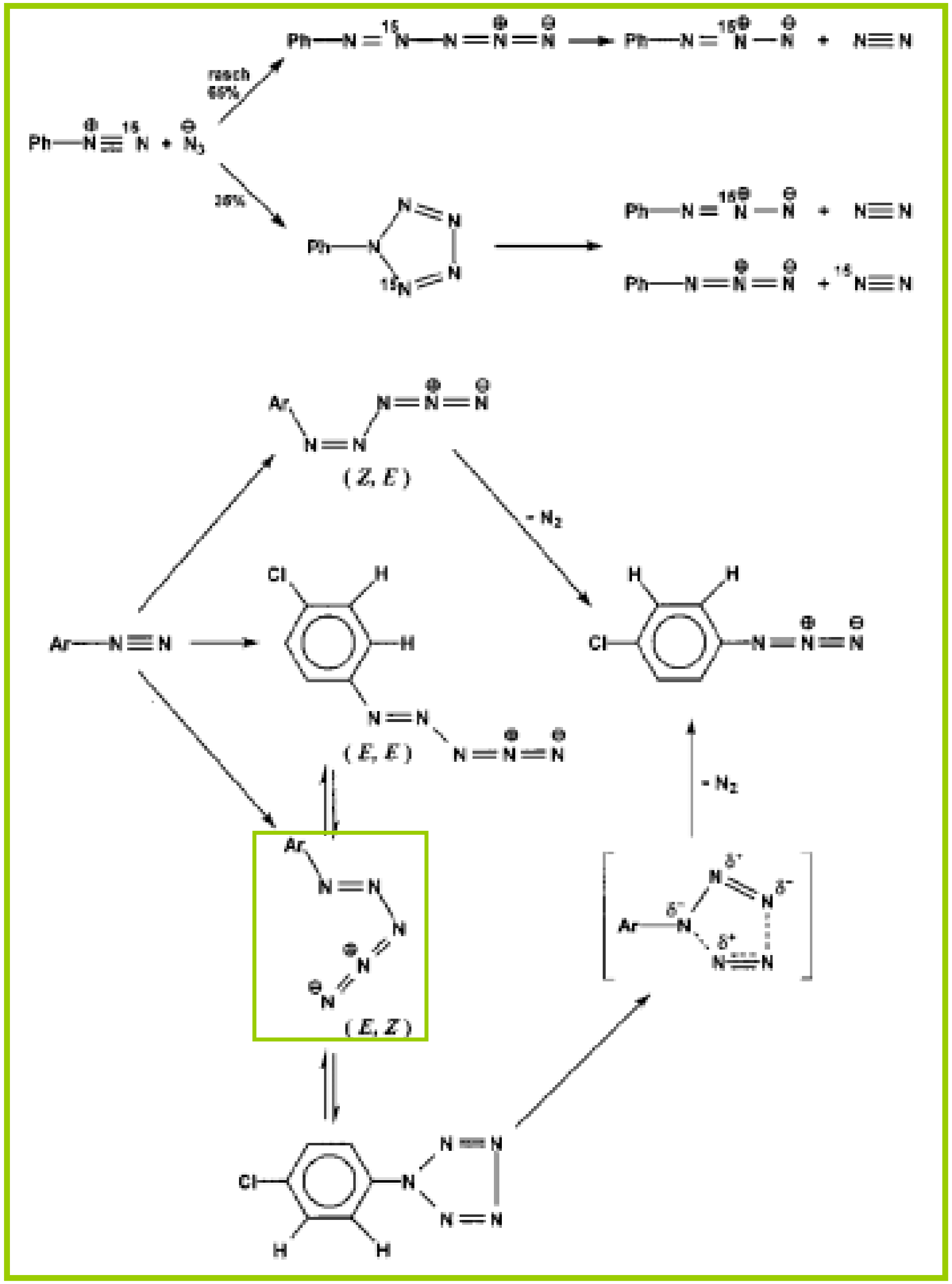
tetrazole azide

Cano Gorini et al., *Chem. Comm.*, 1986, 959.

Proposed Mechanisms of the Reaction of R-N_2^+ with N_3^-



Mechanism proposed by Huisgen & Ugi;
Angew. Chem., 1956, 68, 753.

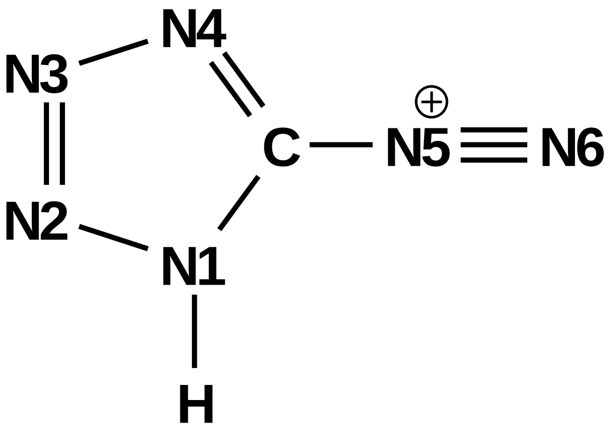


Mechanism proposed by Butler et al., from a theoretical and experimental Study.

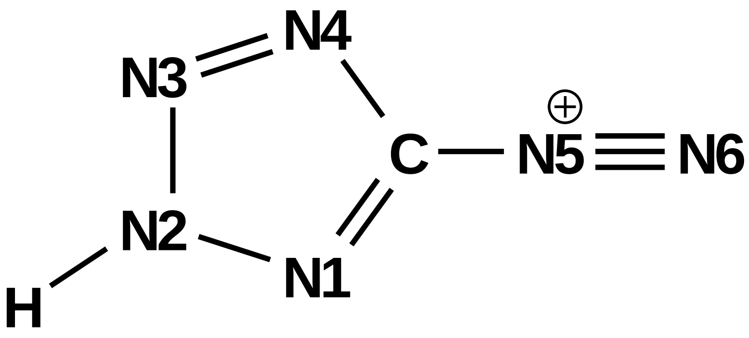
The *(E, Z)*-arylpentazene is a key intermediate in this mechanism

Butler et al. J. Chem. Soc., Perkins Trans., 1998, 2243.

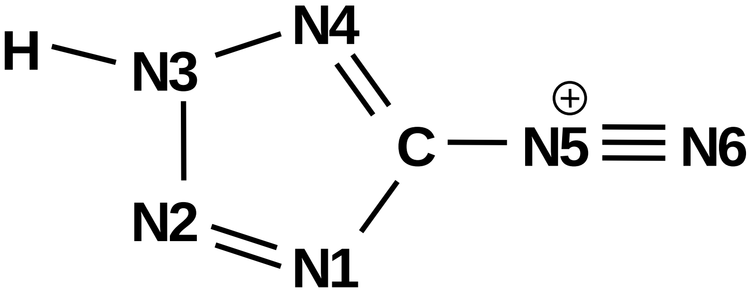
Calculation of Tetrazole Compounds



1*H*-tetrazolediazonium



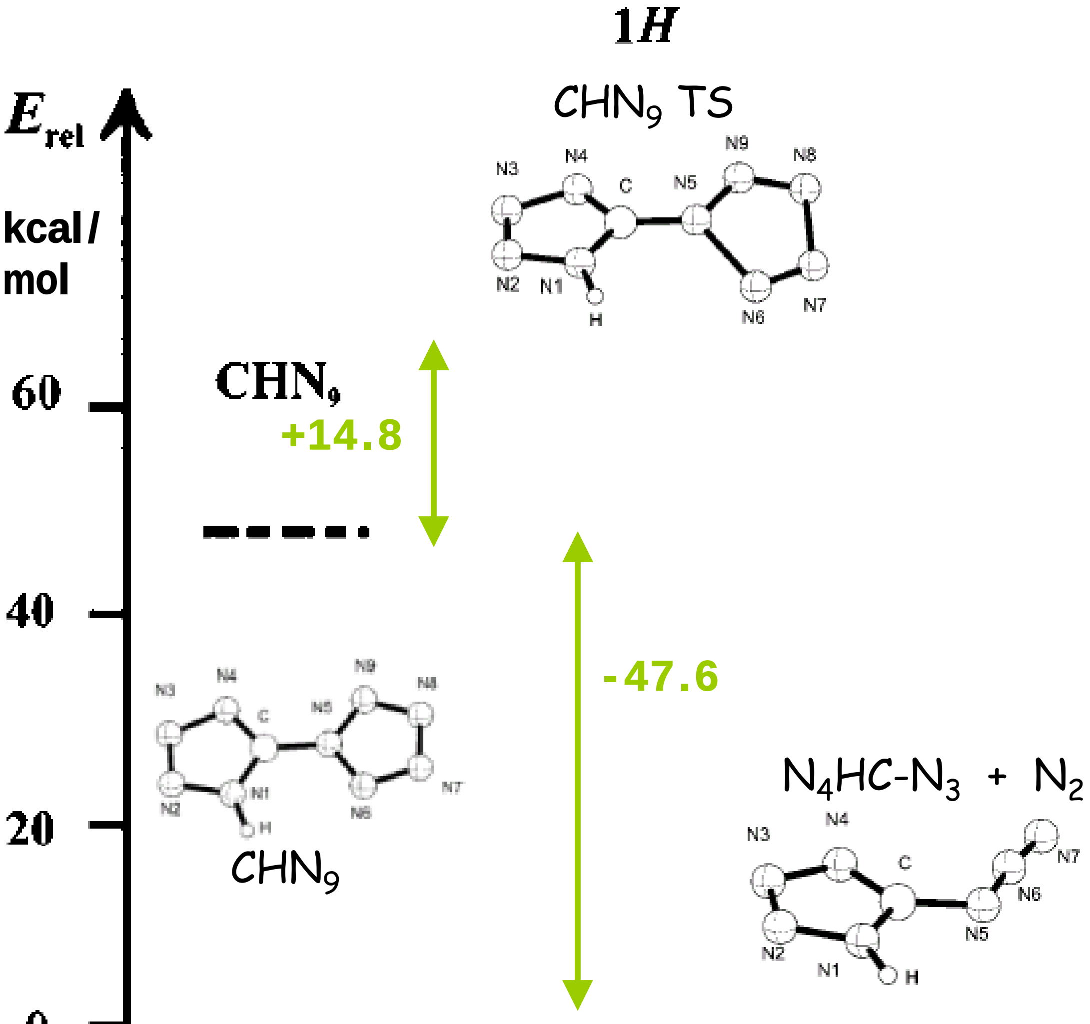
2*H*-tetrazolediazonium

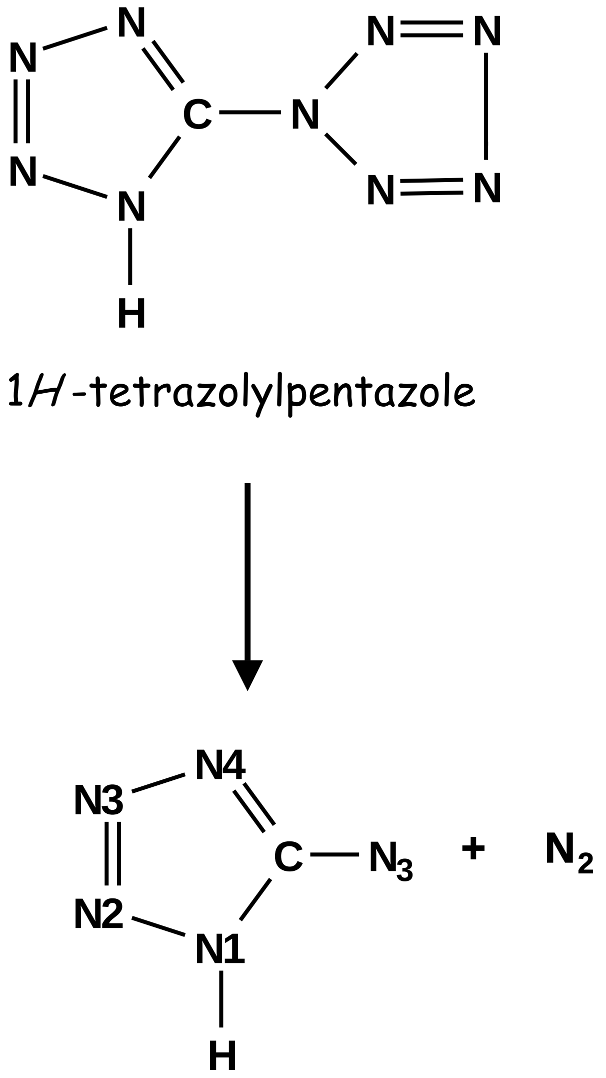


3*H*-tetrazolediazonium

Klapötke et al., *Inorg. Chem.*, 2002, 41, 906.

Decomposition pathway of 1*H*-tetrazolylpentazole



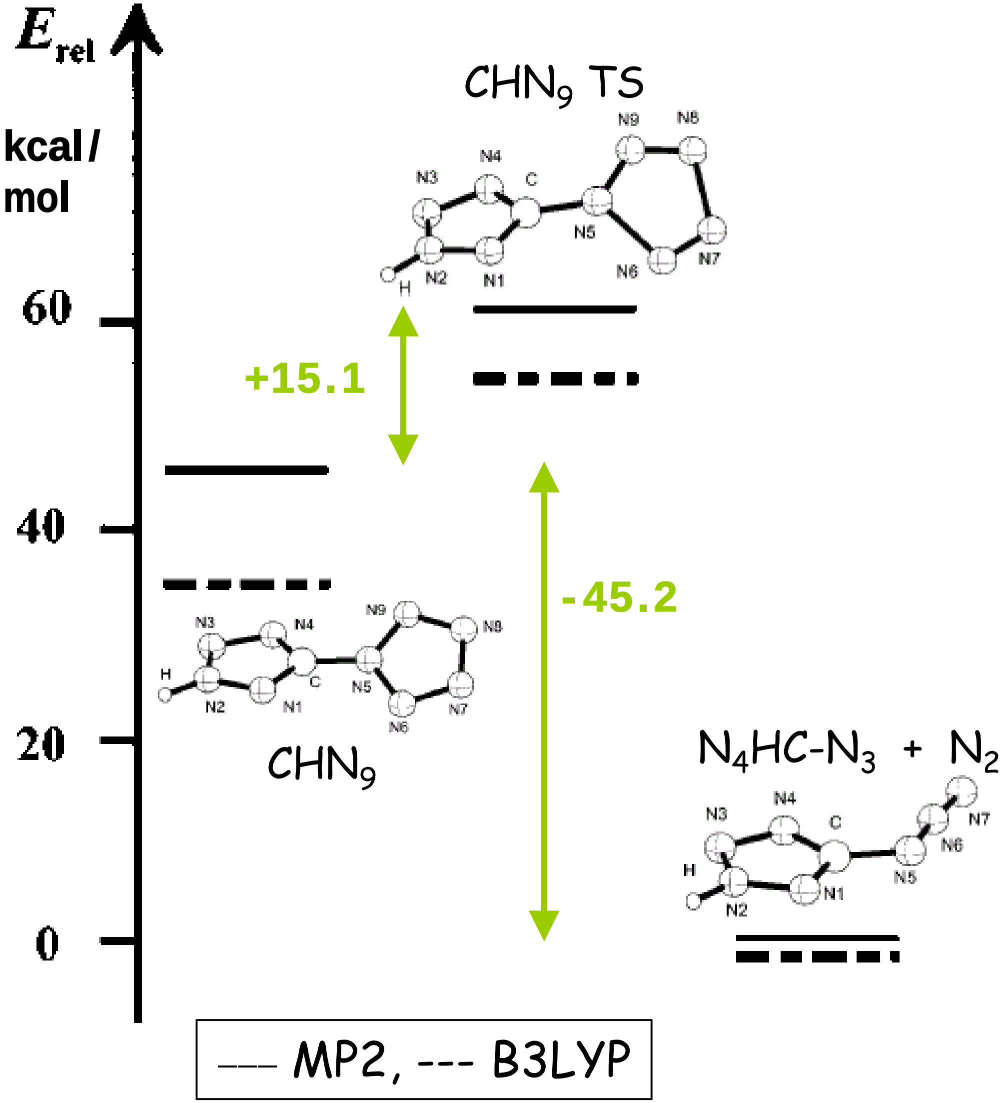


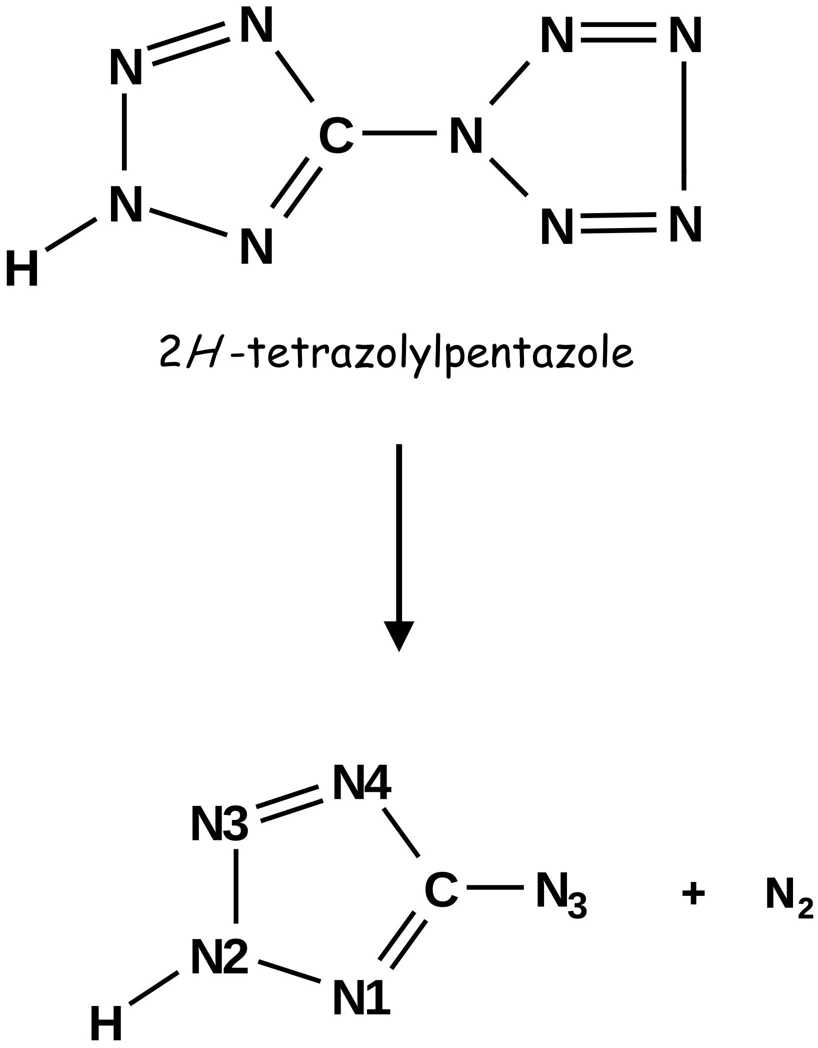
1*H*-tetrazolylpentazole

1*H*–Azidotetrazole + N_2

––– MP2, --- B3LYP

Decomposition pathway of 2*H*-tetrazolylpentazole

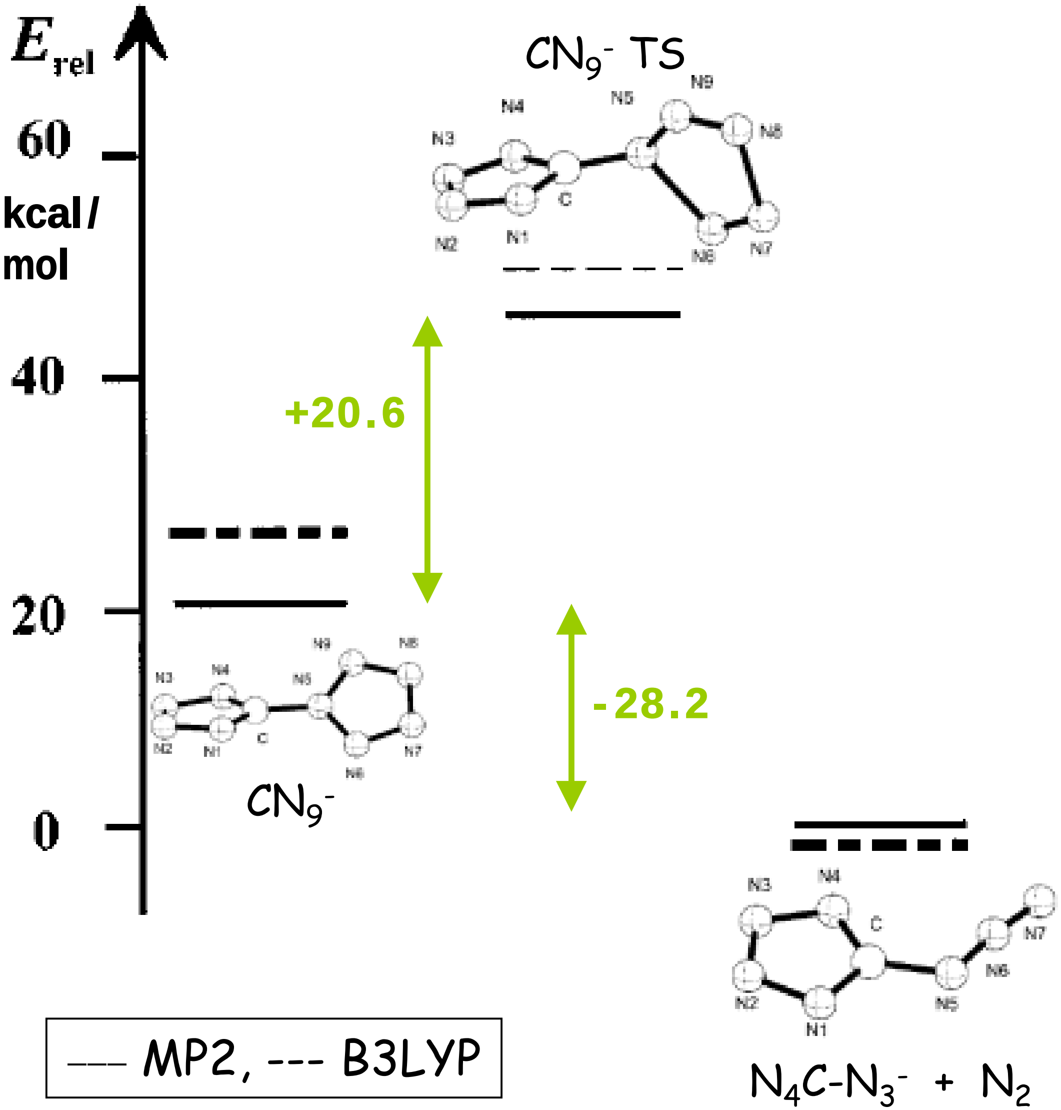


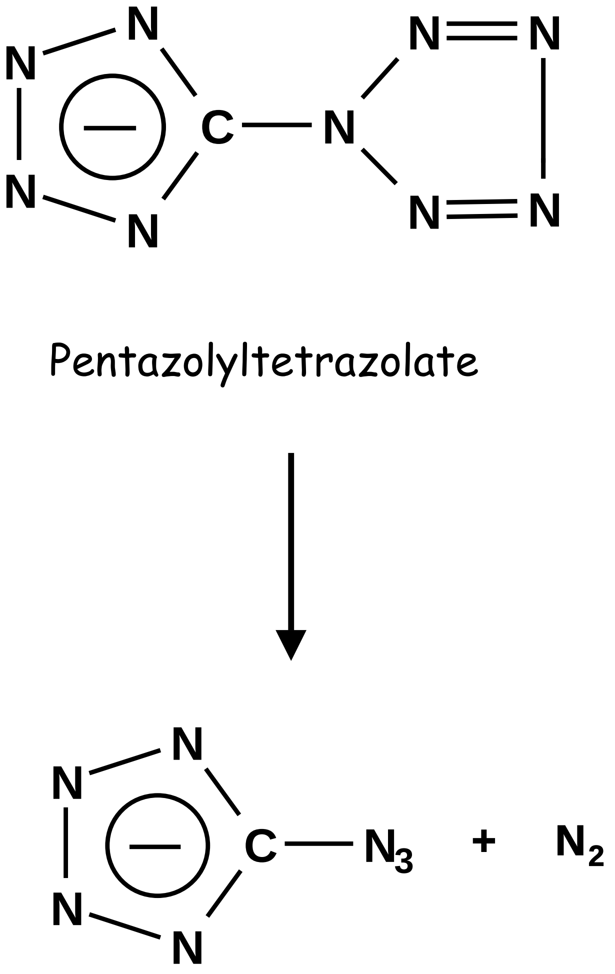


2*H*-tetrazolylpentazole

2*H*–Azidotetrazole + N_2

Decomposition pathway of Pentazolyltetrazolate

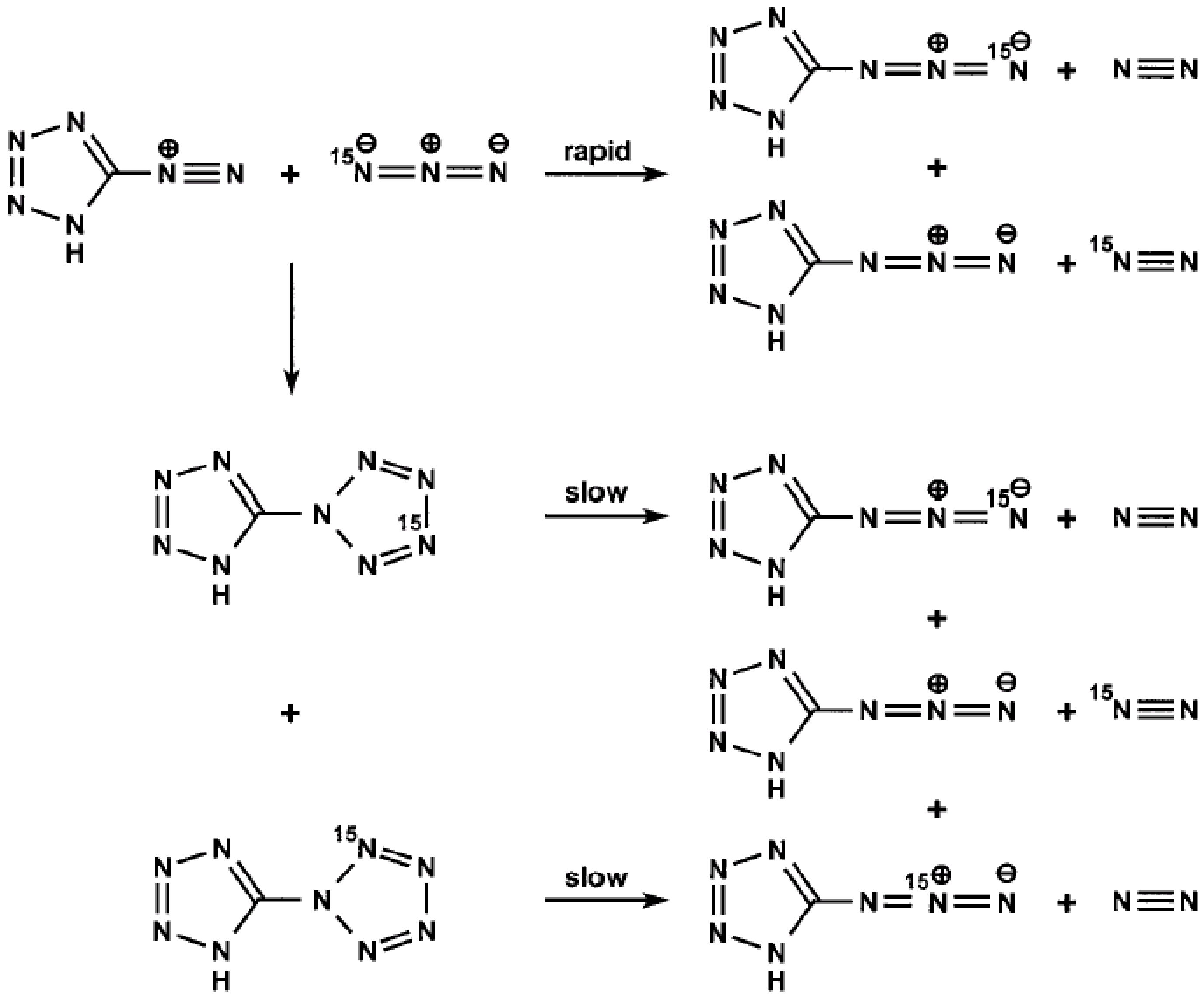




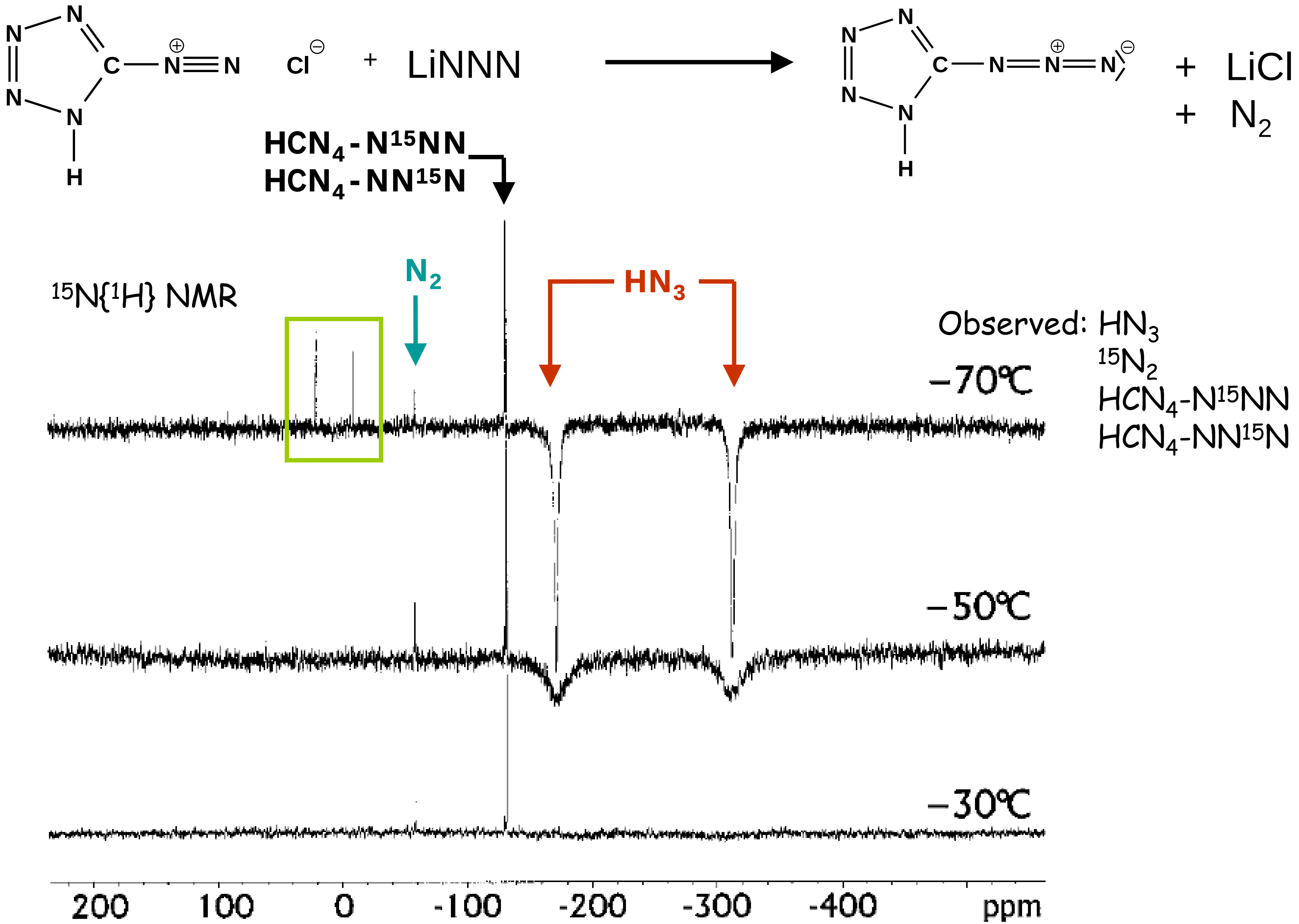
Pentazolyltetrazolate

Azidotetrazolate + N_2

Reaction Pathways for the Reaction of $^{15}NNN^{-}$ with Tetrazolediazonium chloride



Experimental Evidence for the Existence of Tetrazolylpentazole



Observed: HN_3
$^{15}N_2$
HCN_4-$N^{15}NN$
HCN_4-$NN^{15}N$

Electrostatic Potential

$$V(r) = S \{Z_A / (|R_A - r|)\} - ?(?(r')\, dr') / (|r' - r|)$$

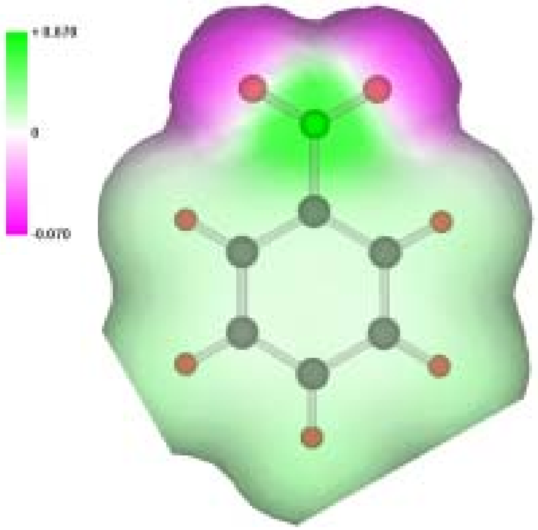
Organic molecules:

Negative regions cover a smaller portion of the total surface area, but are significantly stronger than the **positive** ones.

Energetic molecules:

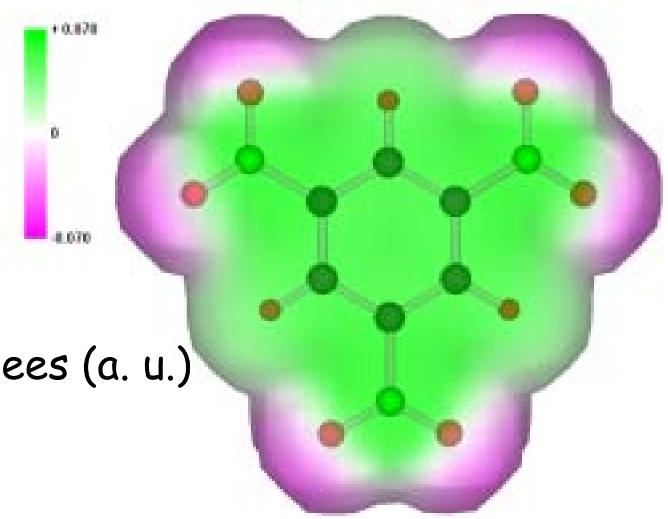
Positive regions are still larger but also now stronger than the **negative**.

P. Politzer *et al.* and B. Rice *et al.* were able to show that impact sensitivity can be expressed as a function of the extent of this anomolous reversal of the strengths of the positive and negative surface potentials.



nitrobenzene

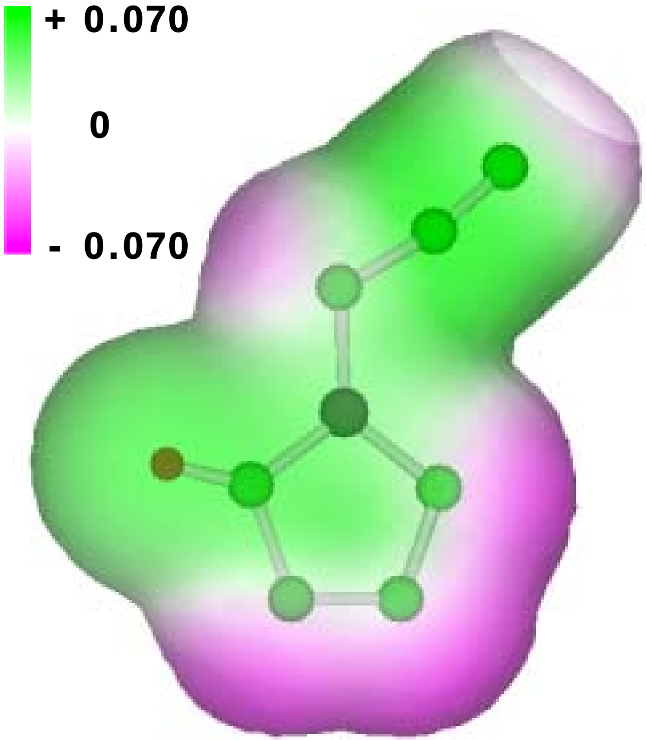
Electrostatic potentials.
Legend for the color ranges of the ESPs ranges
From – 0.07 → + 0.07 hartrees (a. u.)



trinitrobenzene

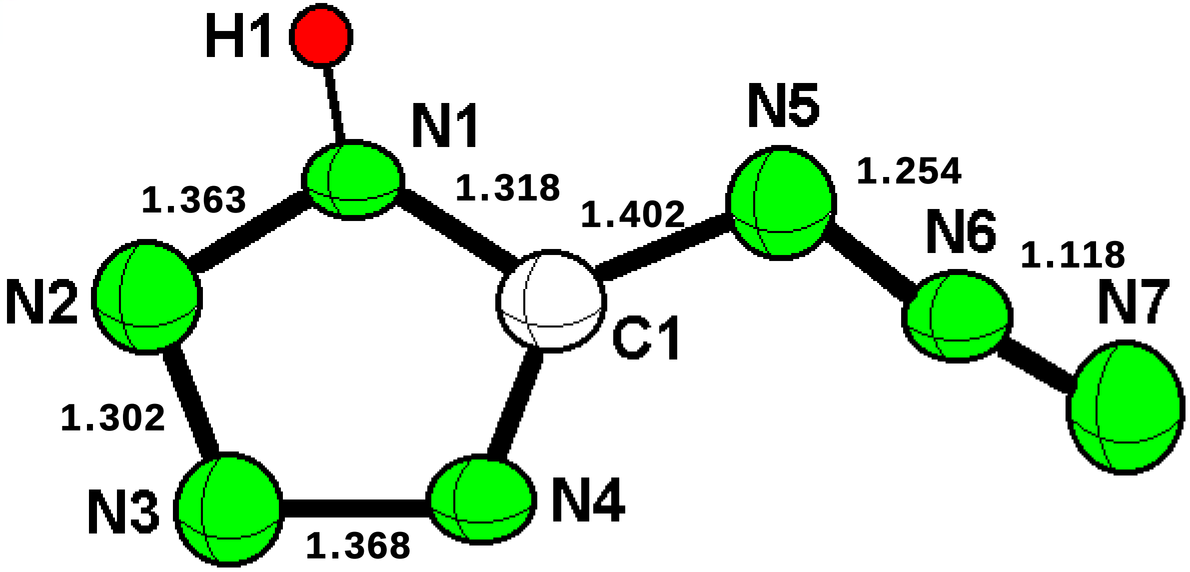
Tetrazoleazide, CHN_7

$CHN_4\text{-}NH_2 + HNO_2 / HCl \rightarrow [CHN_4\text{-}N_2]^+[Cl]^- + 2\ H_2O \xrightarrow{NaN_3} CHN_4\text{-}N_3 + N_2 + NaCl$



Electrostatic potential

Detonation pressure, P = 21.7 GPa
Detonation velocity, D = 7160 ms^{-1}



N content = 88.3 %

monoclinic, *P*1 2_1/*n*1
a = 13.466(5) Å; b = 4.996(2) Å;
c = 13.609(5) Å; ß = 105.14(1)°;
V = 884(2) $Å^3$; *Z* = 8; ρ = 1.670 g cm^{-3}

C1-N5 = 1.402 Å; N5-N6 = 1.254 Å; ∠(N5-N6-N7) = 172.51°;
N6-N7 = 1.118 Å; N1-C1 = 1.318 Å; ∠(C1-N5-N6) = 113.51°;
H1-N1 = 0.772 Å; N1-N2 = 1.363 Å; ∠(N2-N3-N4) = 110.66°;
N2-N3 = 1.302 Å; N3-N4 = 1.368 Å; ∠(N1-C1-N5) = 120.77°.

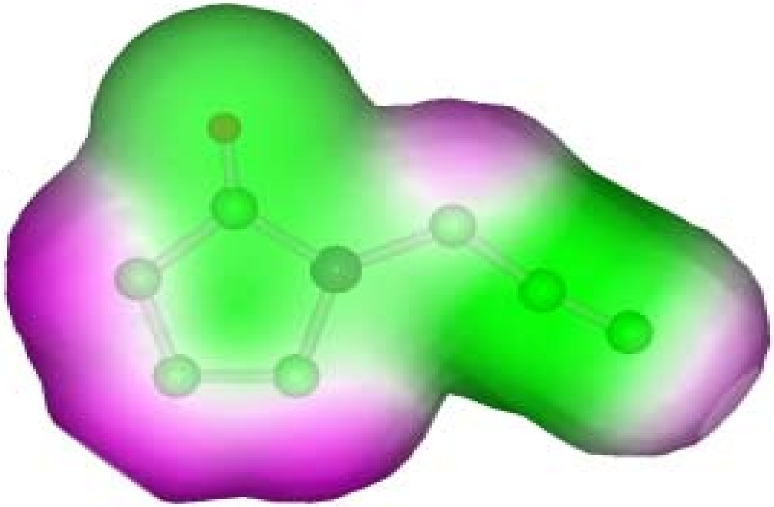
T. M. Klapötke et al., Prop. Expl. Pyrotech. **2003**, *28*, 165.

Electrostatic Potentials of Tetrazole azide, Phenyltetrazol azide, Aminotetrazole and Methylaminotetrazole

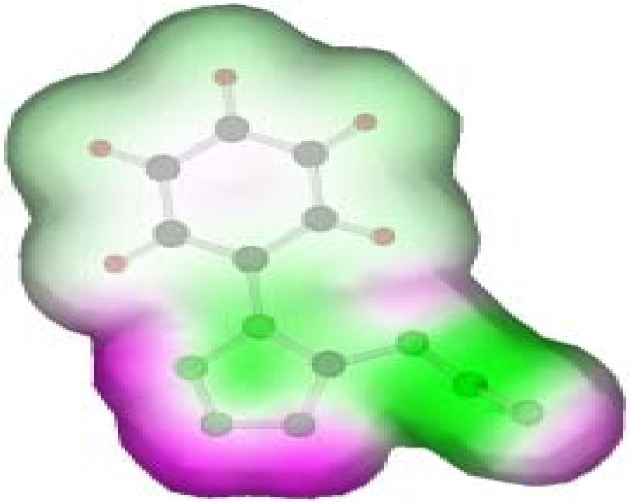
+ 0.070

0

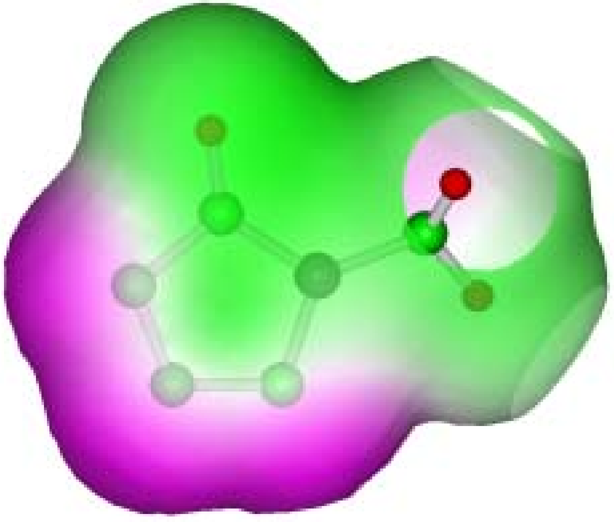
- 0.070



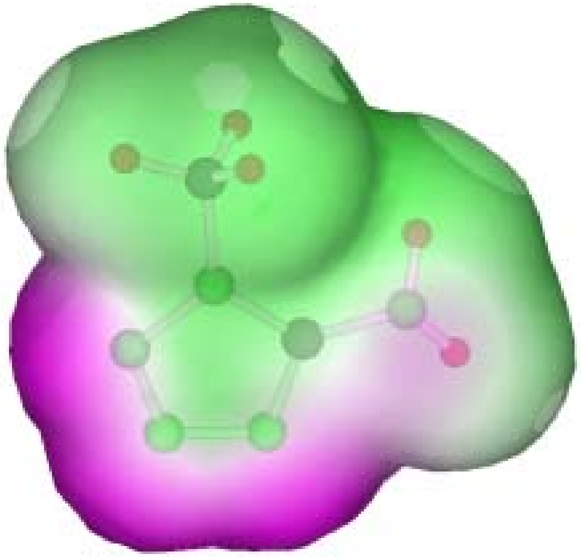
Tetrazole azide



Phenyltetrazol azide

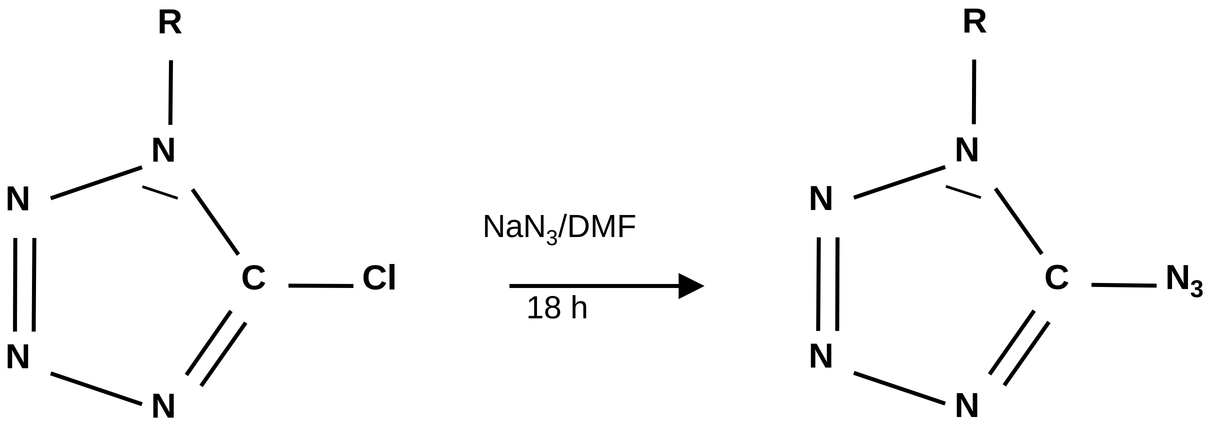


Aminotetrazole

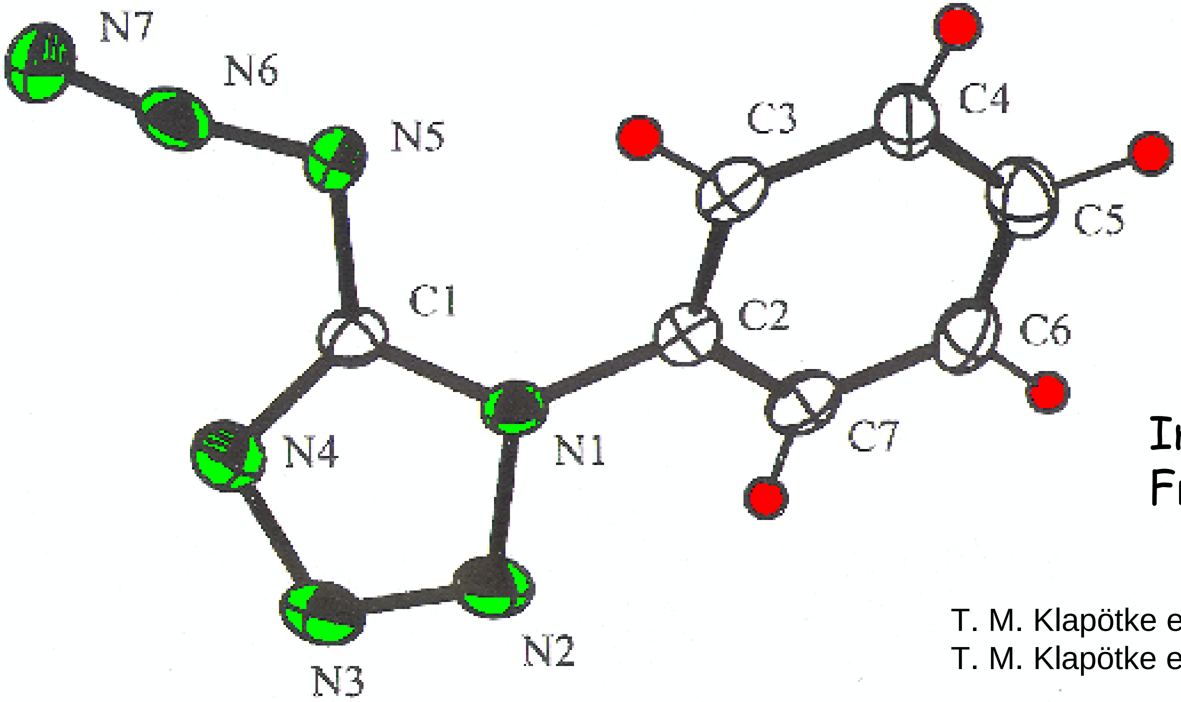


Methylaminotetrazole

Substituted tetrazole azides



R = Me, yield = 50 %
R = Ph, yield = 75 %

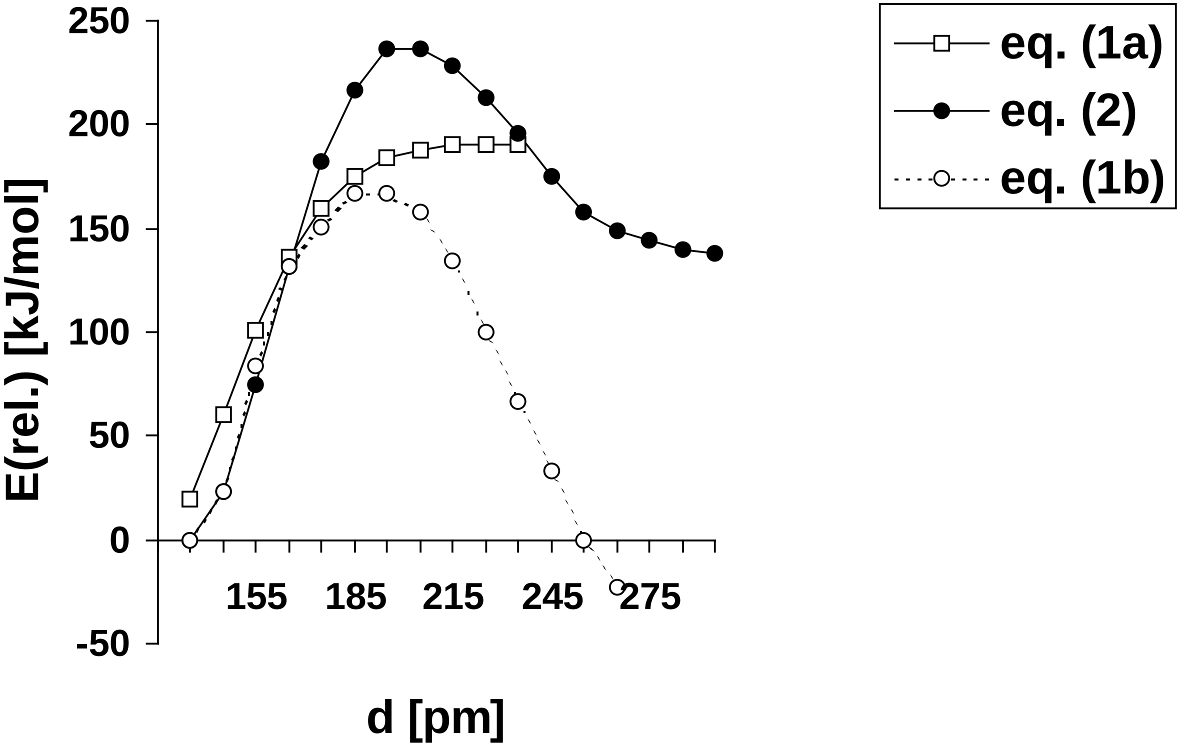


orthorhombic, *Pna*2_1
a = 11.467(2),
b = 3.805(4)
c = 18.808(3)
Z = 4
ρ = 1.515 g cm-3

Impact sensitivity	> 30 Nm
Friction sensitivity	> 180 N

T. M. Klapötke et al., Prop. Expl. Pyrotech., August, 2003.
T. M. Klapötke et al., unpublished

Possible decomposition pathways of tetrazole azide, HCN_7



Two-dimensional energy hypersurface (B3LYP/6-31G(d,p)) showing:

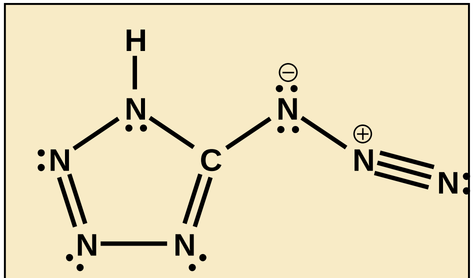
- * the dissociation of **tetrazole azide** into N_2 and CHN_4-N (C_s, eq. 1a, ···?···),
- * the dissociation of **tetrazole azide** into 2 N_2 and N=C-N(H)-N (C_1, eq. 1b, -?-) and
- * the dissociation of **tetrazole azide** into HN_3 and NC-N_3 (eq. 2, -?-).

CHN_4-N_3 → CHN_4-N + N_2 C_s symmetry (1a)

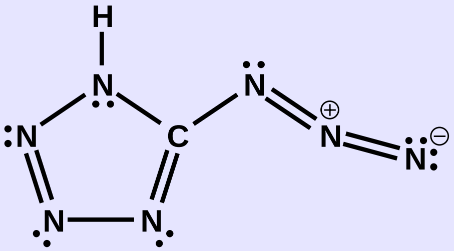
CHN_4-N_3 → N=C-N(H)-N + 2 N_2 C_1 symmetry (1b)

CHN_4-N_3 → NC-N_3 + HN_3 C_s symmetry (2)

Valence Bond Consideration of tetrazoleazide, HCN_7



I



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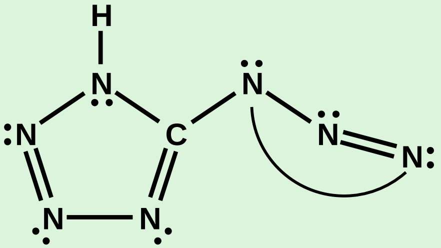

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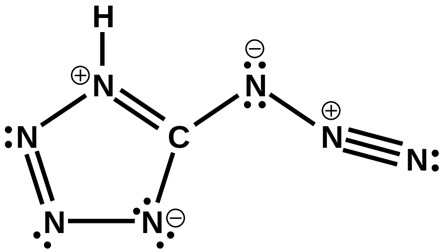

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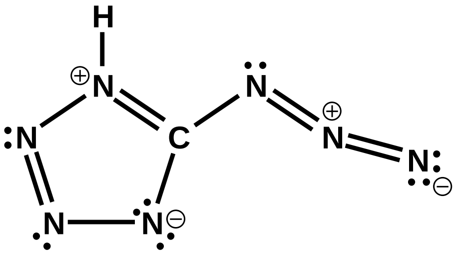

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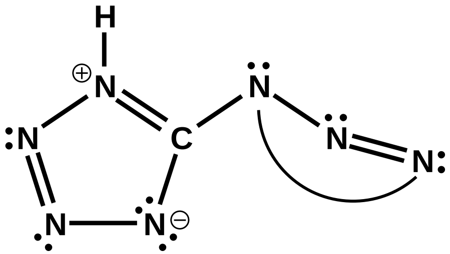
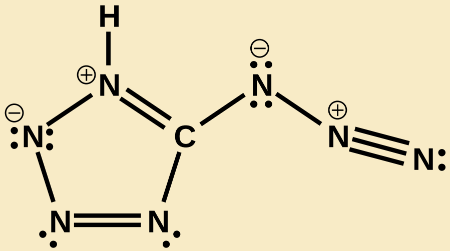
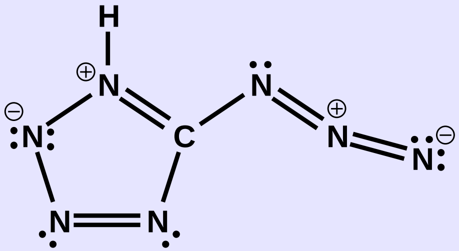


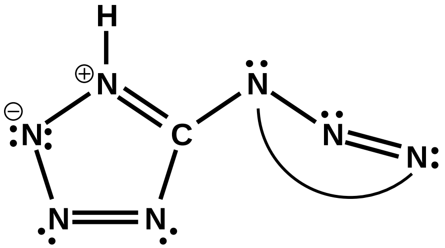
VI



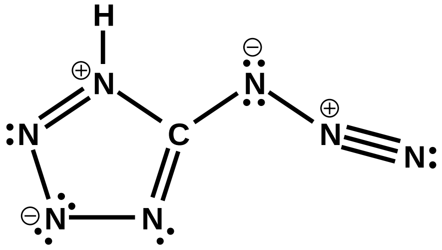
VII



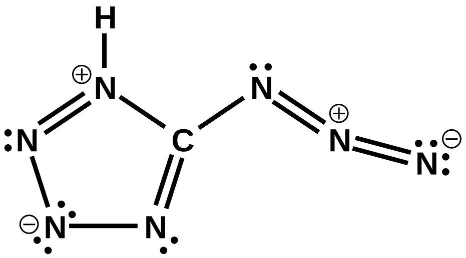
VIII



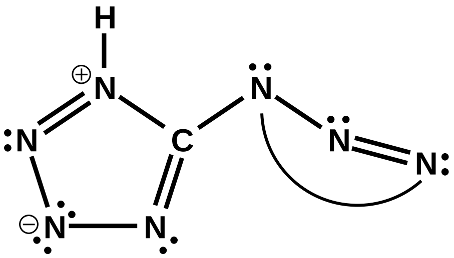
IX



X

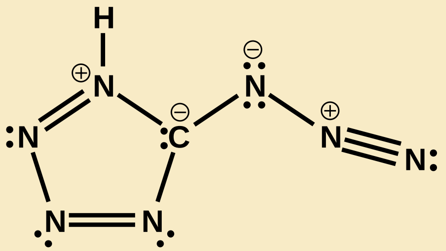


XI

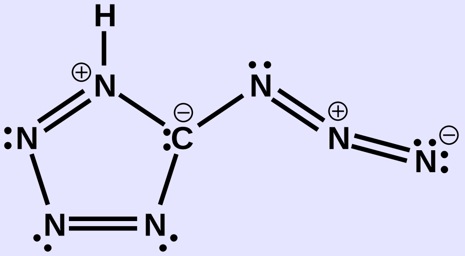


XII

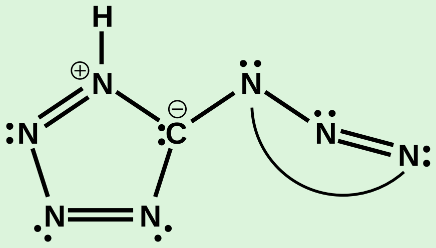
Valence Bond Consideration of tetrazoleazide, HCN_7



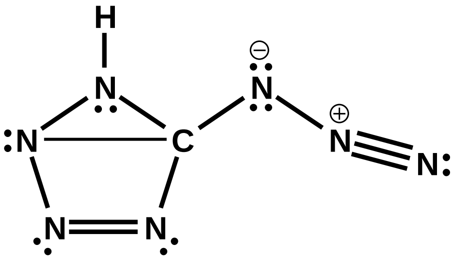
XIII



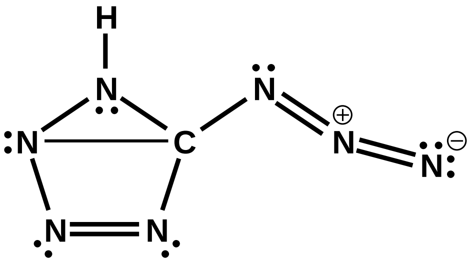
XIV



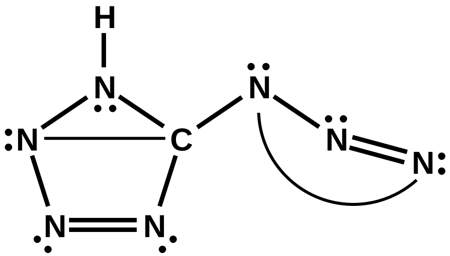
XV



XVI



XVII



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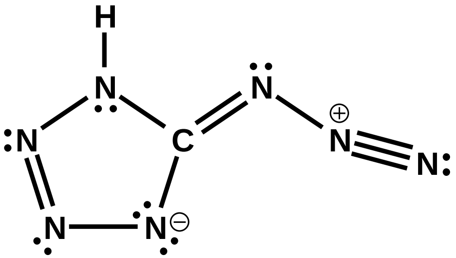
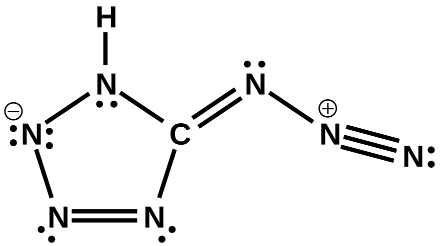
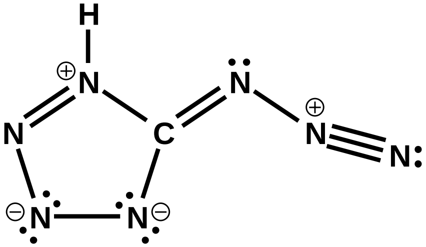


XIX



XX



XXI

VB structure	Structural type	no. formal charges	structural weight (Mulliken type) 6-31G/D95
I	Kekulé	2	0.04 / 0.06
II	Kekulé	2	0.08 / 0.08
III	Dewar (azide)	0	0.03 / 0.04
IV	Kekulé	4	0.02 / 0.04
V	Kekulé	4	0.02 / 0.03
VI	Dewar (azide)	2	0.01 / 0.02
VII	Kekulé	4	0.05 / 0.09
VIII	Kekulé	4	0.09 / 0.10
IX	Dewar (azide)	2	0.04 / 0.05
X	Kekulé	4	0.06 / 0.06
XI	Kekulé	4	0.10 / 0.05
XII	Dewar (azide)	2	0.04 / 0.03
XIII	Kekulé	4	0.08 / 0.07
XIV	Kekulé	4	0.15 / 0.09
XV	Dewar (azide)	2	0.06 / 0.05
XVI	Dewar (tetrazole)	2	0.03 / 0.04
XVII	Dewar (tetrazole)	2	0.06 / 0.05
XVIII	Dewar (azide andtetrazole)	0	0.02 / 0.02
XIX	Kekulé (exocyclic C=N double bond)	2	0.01 / 0.01
XX	Kekulé (exocyclic C=N double bond)	2	0.00 / 0.01
XXI	Kekulé (exocyclic C=N double bond)	4	0.01 / 0.01

Acknowledgments

Research group of Prof. Dr. T. M. Klapötke

- Priv.-Doz. Dr. K. Karaghiosoff
- Dr. M-j Crawford
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- Dr. D. Adam
- Dr. J. Geith
- Dr. A. Hammerl
- Dr. C. M. Rienäcker
- Dipl.-Chem. A. Michailowski
- Dipl.-Chem. I. Schwab
- Dipl.-Chem. J. Weigand
- J. M. Welch, B.A.
- A. Burdzy
- C. Nowak
- G. Spieß

many undergraduate students

Dr. R. D. Harcourt
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Valence Bond, Theory

Prof. Dr. J. Liebman
Univ. Maryland, USA: Theory

Dr. J. Li
SciNet, SanDiego, USA:
VB Theory

Dipl.-Ing. H. Zewen
EADS, Ottobrunn: Propulsion

Dr. G. Holl,
WIWEB, Erding: HEDM

Prof. Dr. H. - G. Ang
NUS, Singapore: HEDM

Prof. Dr. J. M. Winfield,
Univ. Glasgow, Scotland: Catalysis

Research Group of Prof. Dr. Thomas M. Klapötke
Professor of Inorganic Chemistry
http://www.chemie.uni-muenchen.de/ac/klapoetke/index.html

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a past to build a future on

BWB

WIWEB

Wehrwissenschaftliches Institut für
Werk-, Explosiv- und Betriebsstoffe

I am one of those who think like Nobel,
that humanity will draw more good
than evil from new discoveries.

Marie Curie

We will not waver; we will not tire; we will not falter;
***and we will not fail. Peace and freedom will prevail*.**
George W. Bush, 2001

The HSAB-Principle and its Application to Energetic Materials and Systems

Dr. E.-C. Koch

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1st Workshop on Pyrotechnic Combustion Mechanisms
July 10th, The Marriott, Fort Collins, Colorado

Structure:

Introduction

Application to Pyrotechnics

Application to High Explosives

Conclusion

Outlook

The HSAB Principle (I)

Most chemical reactions can be described as generalized acid-base reactions of the type given in the following equation:

A = acid, electron acceptor
$:B$ = base, electron donator
$\Delta H°$ = standard enthaply of formation

$$A + :B = A:B, \Delta H°$$

According to experimental data, one can categorize both acids and bases into two separate classes.

•*Acids with high positive charge and small size, with no unpaired electrons (H^+, Li^+),* ***hard acid***

•Acids with low positive charge and large size, with occasionally unpaired electrons (Cu^+, Cs^+) , **soft acid**

•*Bases with an electron cloud that is difficult to deform chemically and with tight bond electrons (OH^-, F^-),* ***hard base***

•Bases with an electron cloud that is easily to deform chemically and with loose bond electrons (I^-, SCN^-), **soft base**

The following reaction is exothermic:

$$CsF_{(g)} + LiI_{(g)} = CsI_{(g)} + LiF_{(g)}, \Delta H = -71 kJmol^{-1}$$

By way of an example this shows the affinity for the respective classes of acids and bases.

The HSAB Principle (II)

From the aforementioned observations and considerations Pearson in 1963 derived the concept of hard and soft acids and bases, the **HSAB Principle**.

In accordance to it qualitatively describes the fact that reactions of the type given below are likely to occur

$$h_A s_B + s_A h_B = h_A h_B + s_A s_B , \Delta H^\circ < 0$$

h = hard
s = soft
And the indices referring to
A= acid
B = base

Hard bases prefer to bound to hard acids and soft bases prefer to bound to soft acids.

The term **hard** refers to the fact that the electron cloud of a hard base is **not easily deformed** thus **hard**; whereas **soft** refers to the electron cloud of a soft base that is **easily deformed** thus **soft**.

hh combinations have high ionic bonding contribution, whereas (LiF)
ss combinations have high covalent bonding contribution (CsI)

$$CsF_{(g)} + LiI_{(g)} = CsI_{(g)} + LiF_{(g)} , \Delta H = -71 kJmol^{-1}$$

Density Functional Theory (I)

A chemical system may comprise several nuclei and N electrons. The nuclei then yield a potential v. If the nuclei are fixed, the ground state electron density function σ, is that satisfies the variational equation:

$$\delta\left[E[\rho]-\mu N[\rho]\right]=0$$

E = total electronic energy
N = number of electrons
μ = the Lagrange multiplier that ensures that the integral of σ over the volume is equal to N. From this it follows that

$$\mu=\left|\frac{\delta E[\rho]}{\delta\rho}\right|_v=v(r)+\left|\frac{\delta F[\rho]}{\delta\rho}\right|_v$$

$F[\sigma]$ = kinetic, electron-electron-repulsion and exchange correlation energy
Since E is a function of N and v only this can be rewritten as:

$$dE=\mu dN+\langle\rho dv\rangle$$

From this the new relationship follows:

$$\mu=\left(\frac{\partial E}{\partial N}\right)_v=-\chi$$

In analogy to thermodynamics the quantity $\boldsymbol{\mu}$ is now called **electronic chemical potential**.

Density Functional Theory (II)

$$\mu = \left(\frac{\partial E}{\partial N}\right)_v \approx \frac{I + A}{2} = -\chi_M$$

In this context χ_M describes the absolute electronegativity (Mulliken - electronegativity). I and A designate the ionization energy and the electron affinity of the corresponding specie. The **chemical hardness** η then describes the resistance of the electronic potential with respect to a change in the number of electrons. It is related to the electronic chemical potential as follows:

$$\eta = -\frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_V \approx \frac{I - A}{2}$$

For isolated reactants, A and B it follows that

$$\mu_A = \mu_A^0 + 2\eta_A \Delta N, \mu_B = \mu_B^0 - 2\eta_B \Delta N$$

Whith ΔN the fractional number of electrons transferred from B to A. In case of $\mu_A=\mu_B$, it can be found that

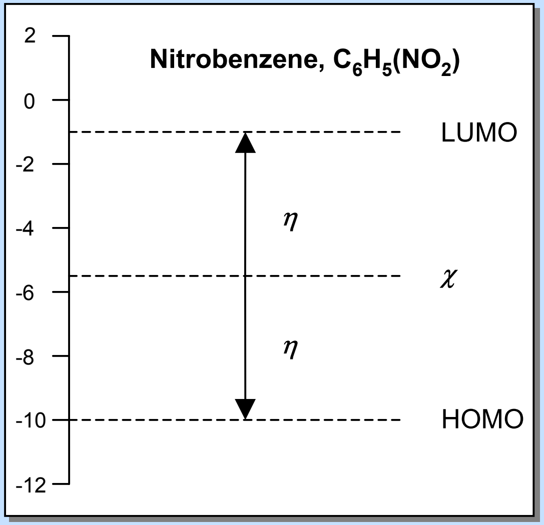
$$\Delta N = \frac{\left(\chi_A^0 - \chi_B^0\right)}{2\left(\eta_A + \eta_B\right)}$$

Thus the difference in EN drives the reaction, and the sum of the hardness parameters acts as a resistance against it.

Correlation of HSAB-Principle to MO Theory

Although it was *Pearson* who introduced the HSAB principle to chemistry it was not until *Parr* (*1983*) that the more or less qualitative terms **hard** and **soft** could be expressed numerically by means of the relations given before.

Looking at MO theory *hard* vs.*soft* is based on the relative magnitude of the band gap η, between HOMO und LUMO. Thus a system is considered **hard** if η is large.



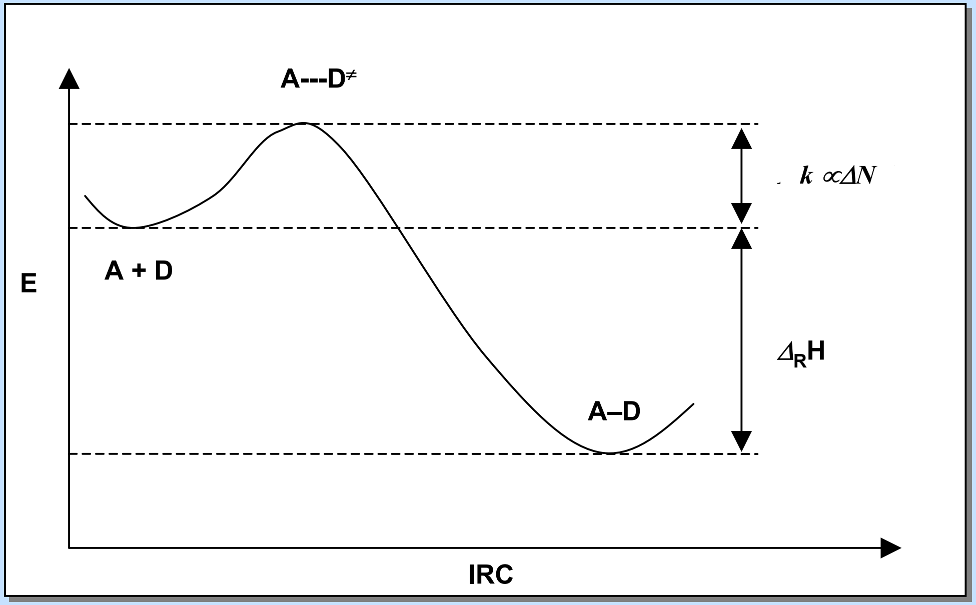
Acid-Base Reactions

The value ΔN shown before correlates very well with the equilibrium constants of a corresponding such as:

$$A + :B = A:B,\ \Delta H^\circ$$

$$\Delta N = \frac{\chi_A - \chi_D}{2 \cdot (\eta_A + \eta_D)}$$

This equation is phenomenological equivalent to Ohms law
(U/R = I).



Application to Pyrotechnics: Performance

The properties and performance of homogeneous energetic materials such as high explosives are easily described and predicted applying the functional relations discovered by Kamlet & Jacobs making use of the explosion enthalpy and the density of the materials.
One of the challenging tasks in the development of new pyrotechnics but also understanding of common pyrotechnic systems is the prediction and explanation of the performance of a given system.
The performance of an energetic material or system is given by the simple relationship

$$\boxed{I = \dot{m} \cdot E}$$

with:
E = the specific reaction enthalpy (combustion or explosion enthalpy) [J g^{-1}], and
$\dot{m}$ = the mass consumption rate [g s^{-1} cm^{-2}].

Unlike with high explosives the mass consumption rate of pyrotechnics as one of the key peformance figures is not direct accessible. Hence the mass consumption rate of these systems has been phenomenologically described using experimentally obtained data as with e.g. metal/nitrate, metal/perchlorate, metal/fluorocarbon systems.
Although models exist, these are not straightforwardly applied to new systems and hence prediction is impeded.

Application to Pyrotechnics: Performance

To set up a model for understanding the reactivity of pyrotechnics requires knowledge of the mechanistic steps determining the rate of reaction.

Since the 1960s extensive use of thermoanalytical methods on pyrotechnics has revealed the importance of the so-called pre-ignition-reaction (PIR) occuring in the condensed phase. Thus it is generally acknowledged that these reactions most often comprise the rate determining step (McLain, 1983). Surprinsingly no or at least only scarce use of this concept has been made to understand and predict the performance of pyrotechnics. As a matter of fact development of pyrotechnics today still relies mainly on intuition and emprirical knowledge.

While investigating the performance of hitherto unknown fluorocarbon oxidizers in metal/pyrolant systems the author made use of this concept with considerable success.

The general reaction taking place in stoichiometrically balanced magnesium/fluorocarbon pyrolants is given below.

$$2\overbrace{Mg}^{0} + \frac{4}{m}\overbrace{C_nF_m}^{\Delta_F H_{298}} \longrightarrow 2\overbrace{MgF_2}^{-1124} + \frac{4}{m}\cdot n\overbrace{C}^{0}$$

$$\Delta_R H_{298} = \left(2\cdot 1124 - \frac{4}{m}\cdot \Delta_F H_{298}\right) kJ$$

Metal + Halocarbons (I)

Davis developed the mechanistic concept, that the rate of reaction of magnesium/fluorocarbon pyrolants is mainly influenced by the following reaction step.

$$R_3C - F + Mg \xrightarrow{\Delta} R_3C - Mg - F$$

Liu & Davis (1991-94)

The intermediary Grignard compound have been observed upon co-condensaton reactions of Mg and $C_nH_mX_z$ species (Sergeev, 1982, Andrews 1998) as well as in Mg/PTFE (Koch, 2002) and most recently in Zn/PTFE pyrolants (Koch, 2004).

Liu & Davis calculated the activation energy for the insertion of the magnesium into the C–F –bond of methylfluoride (CH_3F), fluoroethylene (C_2H_3F) and tetrafluoroethylene (C_2F_4) using ab-initio theory.

Although the applied methods allow for comparingly high reliability it is obvious that such calculations become impractical in case of multi-atom systems since computer time rises with number of electrons n^4. In addition to render such an approach applicable to researchers not having access to sophisticated quantum chemical methods one should have a reliable mathematical tool allowing spread sheet calculations with accessible values from common chemical reference literature.

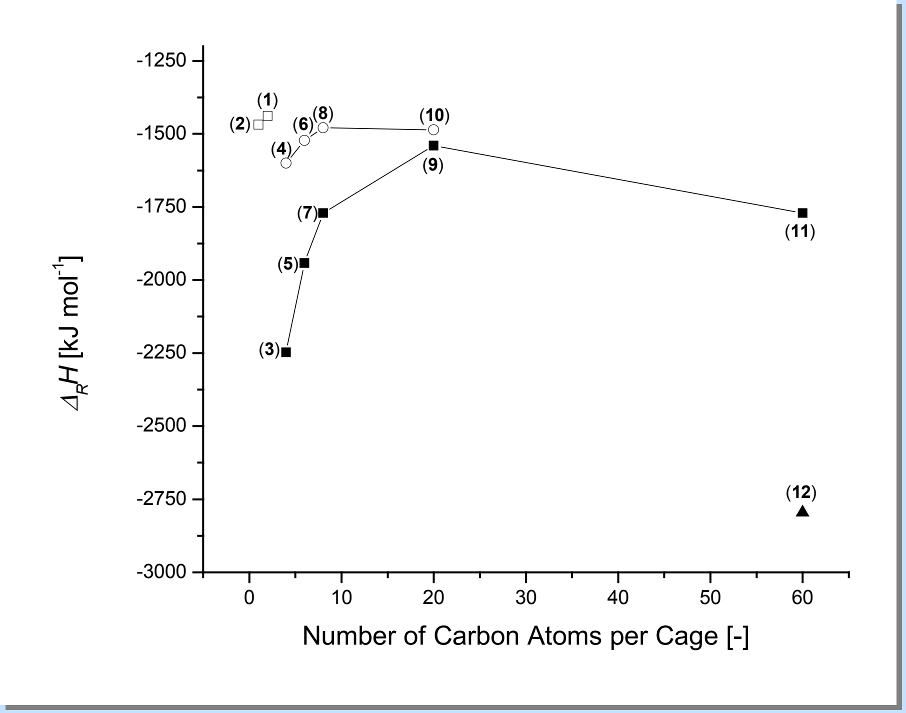
For this purpose the above reaction was considered an acid-base reaction of the type described earlier

$$A + :B = A:B$$

with

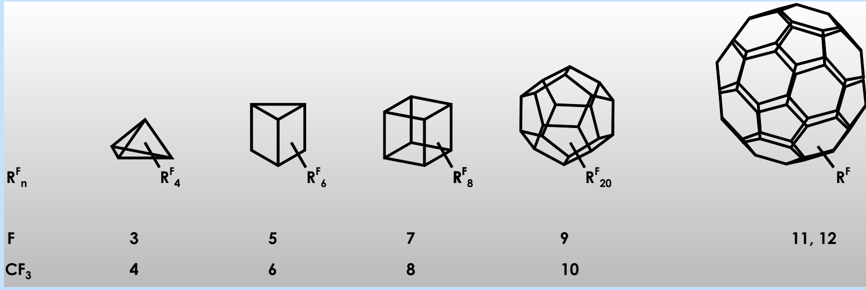
$A = C_nF_m$ and $B = Mg$ and $A:B = C_nF_{m-1}\text{-}Mg\text{-}F$

Metal Halocarbons (II)



The molar reaction enthalpy is maximum with highly strained carbon frameworks! (Koch, 2003)

But what about the rate of reaction expressed by $\dot{m}$?



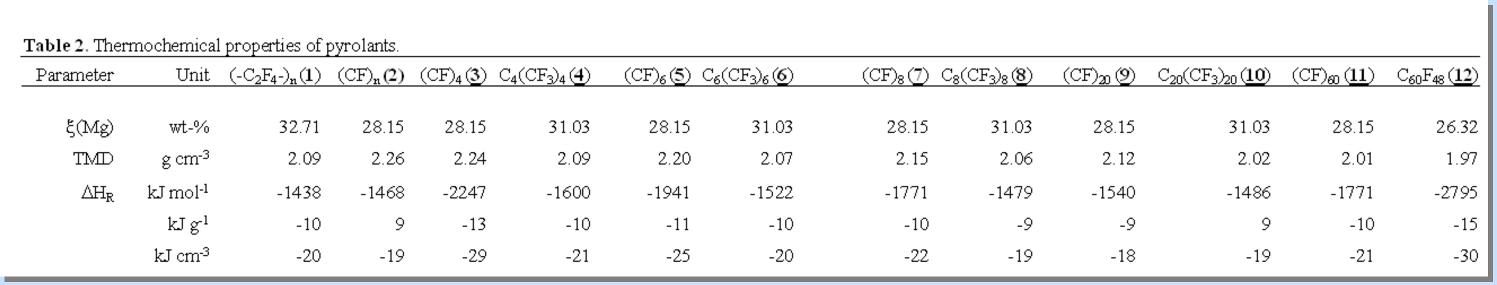
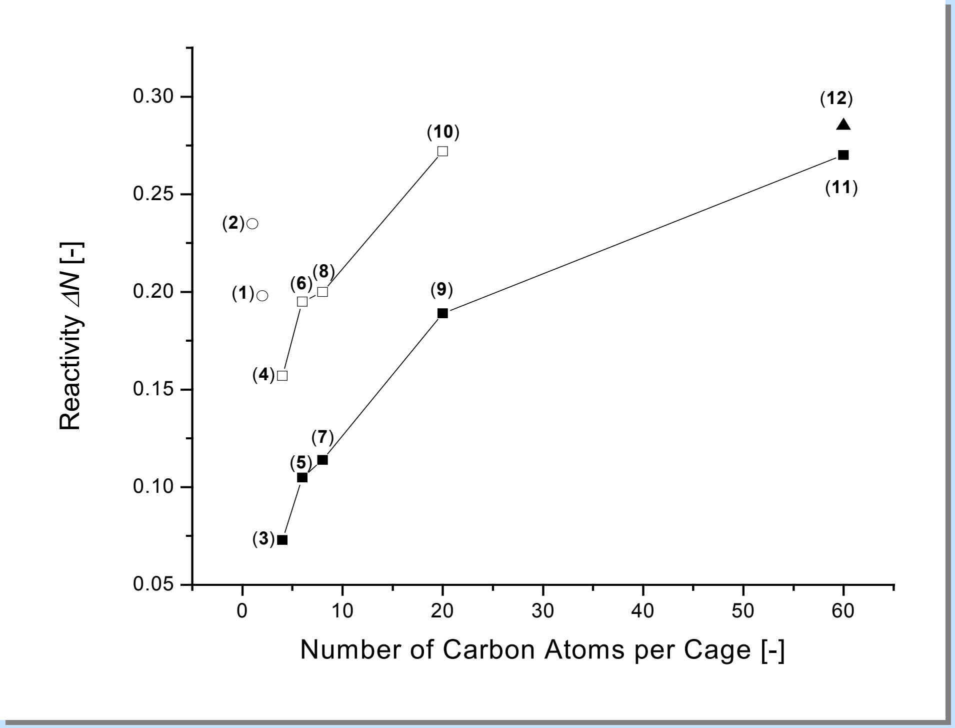


Table 2. Thermochemical properties of pyrolants.

Parameter	Unit	$(-C_2F_4-)_n$ (**1**)	$(CF)_n$ (**2**)	$(CF)_4$ (**3**)	$C_4(CF_3)_4$ (**4**)	$(CF)_6$ (**5**)	$C_6(CF_3)_6$ (**6**)	$(CF)_8$ (**7**)	$C_8(CF_3)_8$ (**8**)	$(CF)_{20}$ (**9**)	$C_{20}(CF_3)_{20}$ (**10**)	$(CF)_{60}$ (**11**)	$C_{60}F_{48}$ (**12**)
ξ(Mg)	wt-%	32.71	28.15	28.15	31.03	28.15	31.03	28.15	31.03	28.15	31.03	28.15	26.32
TMD	g cm^{-3}	2.09	2.26	2.24	2.09	2.20	2.07	2.15	2.06	2.12	2.02	2.01	1.97
ΔH_R	kJ mol^{-1}	-1438	-1468	-2247	-1600	-1941	-1522	-1771	-1479	-1540	-1486	-1771	-2795
	kJ g^{-1}	-10	9	-13	-10	-11	-10	-10	-9	-9	9	-10	-15
	kJ cm^{-3}	-20	-19	-29	-21	-25	-20	-22	-19	-18	-19	-21	-30

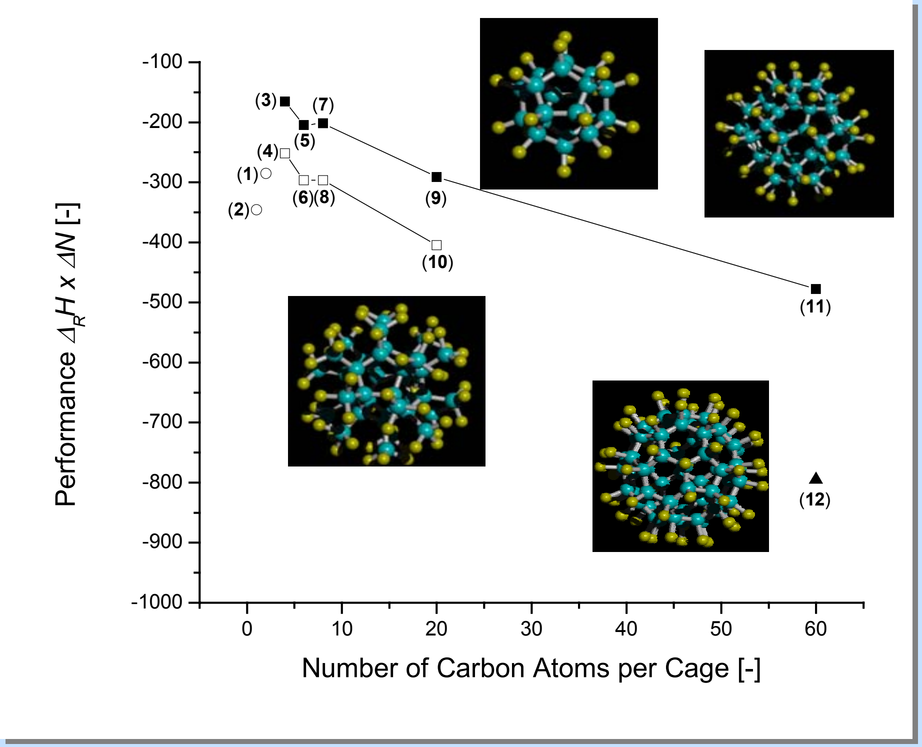
Metal Halocarbons (III)



The compounds displaying highest reactivity are those having local planarity (**9**, **11**, **12** bzw. **10**).
This local geometry causes strong van-der-Waals- strains thus weakening the C-F-bonds, resukting in high reactivity. For compound **12** it was reported in the literature that it hydrolyses upon contact with water (*Kroto, 1992*)).

$$\Delta N = \frac{\chi_{C_nF_m} - \chi_{Mg}}{2 \cdot \left(\eta_{C_nF_m} + \eta_{Mg}\right)}$$

Metal Halocarbons (IV)



The highest relative performance, indicated by large negative values, are the systems with the highest reactivity thus compensating for comparingly lower values of the reaction enthalpy.

Comparison of PTFE (**1**) and PMF (**2**) (see Poster # IPS main event) shows that this description is in good accord with the actual values.

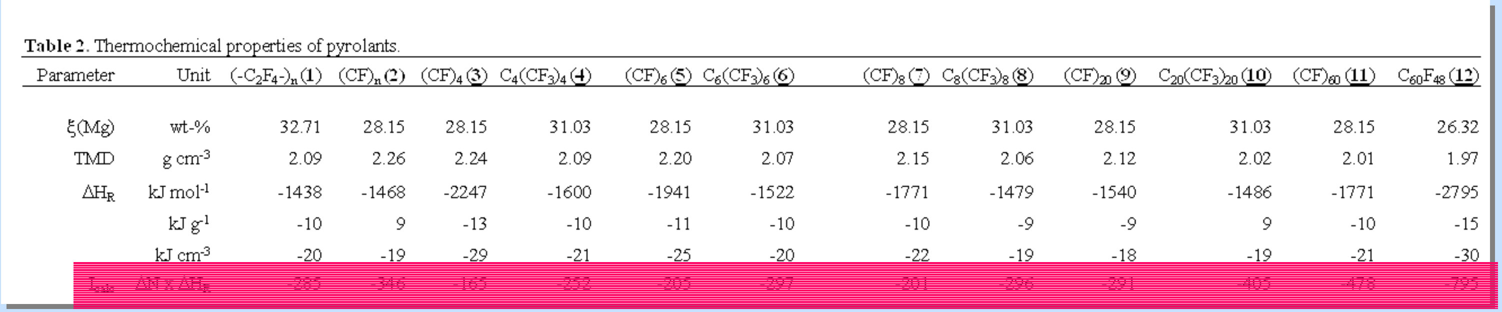


Table 2. Thermochemical properties of pyrolants.

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ξ(Mg)	wt-%	32.71	28.15	28.15	31.03	28.15	31.03	28.15	31.03	28.15	31.03	28.15	26.32
TMD	g cm^{-3}	2.09	2.26	2.24	2.09	2.20	2.07	2.15	2.06	2.12	2.02	2.01	1.97
ΔH_R	kJ mol^{-1}	-1438	-1468	-2247	-1600	-1941	-1522	-1771	-1479	-1540	-1486	-1771	-2795
	kJ g^{-1}	-10	9	-13	-10	-11	-10	-10	-9	-9	9	-10	-15
	kJ cm^{-3}	-20	-19	-29	-21	-25	-20	-22	-19	-18	-19	-21	-30
I_{calc}	ΔN x ΔH_R	-285	-346	-165	-252	-205	-297	-201	-296	-291	-405	-478	-795

Application to High Explosives: Impact Sensitivity

A main challenge upon development of new high explosives is the design of properties such as density and enthalpy of formation and sensitivity. As a matter of fact many developments driven from thermodynamic considerations such as the synthesis of CL-20 and the race to Octanitrocubane now become obvious to have been led in the wrong direction because inherent sensitivity certainly rules any long term application out. (Exceptions e.g. experimental propellant for High velocity missile HFK based on CL-20).

Hence present development mainly must take into account sensitivity considerations. With respect to macro scale sensitivity several researchers have developed models to explain these properties on basis of molecular structure. Politzer *(1990)* in this context has found a relation between the impact sensitivity and the elektrostatic potential of the C–NO_2 bond $V_{mid,max}$.

$$V_{mid} = \frac{Q_C}{0.5R} + \frac{Q_N}{0.5R}$$

$Q_{C,N}$ = Charge of carbon- and nitrogen atom
R = bond length C-N

The „first reaction“ upon impact and shock is often the breakage of the C–NO_2 or N–NO_2-bond (*Owens*).

Exceptions include bond fission in in heterocyclic systems or the decomposition of labile groups such as –N_3 or –N_2– .

Generally the decomposition can be described as follows:

$$R_3C - NO_2 \xrightarrow{impact,shock} R_3C\bullet + \bullet NO_2$$

Impact sensitivity (I)

Beside the work of Politzer many other correlations between sensitivity and experimentally derived parameters have been found. These include:

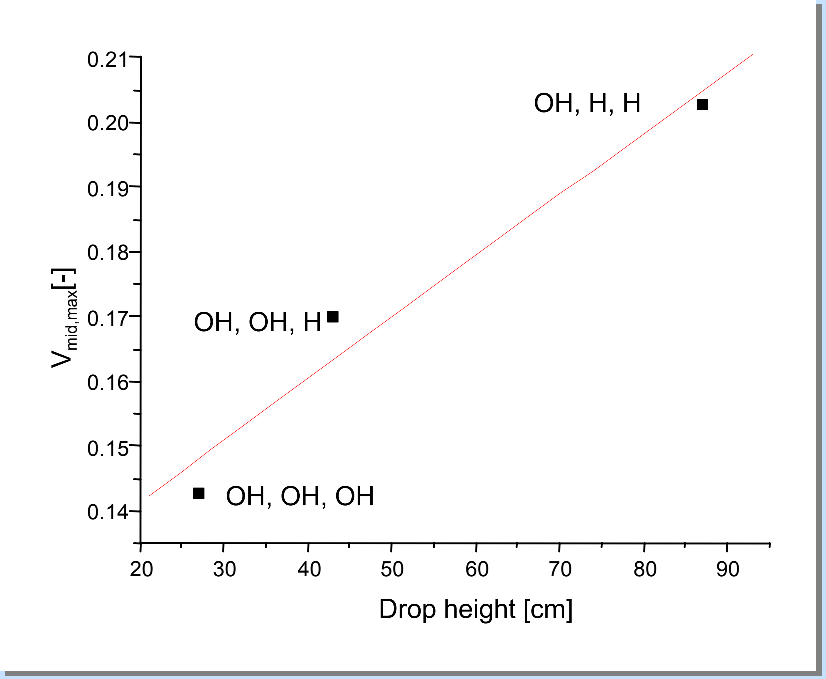
- Oxygen balance *(Kamlet)*
- Enthalpy of fusion (Zeemann)
- ^{14}N bzw. ^{13}C-NMR-Shift (Zeemann)
- E_A of the thermal decomposition reaction (Zeemann)

For modelling new compounds experimental parameters are quite inappropriate, since those are not accessible and require the perhaps cumbersome synthesis

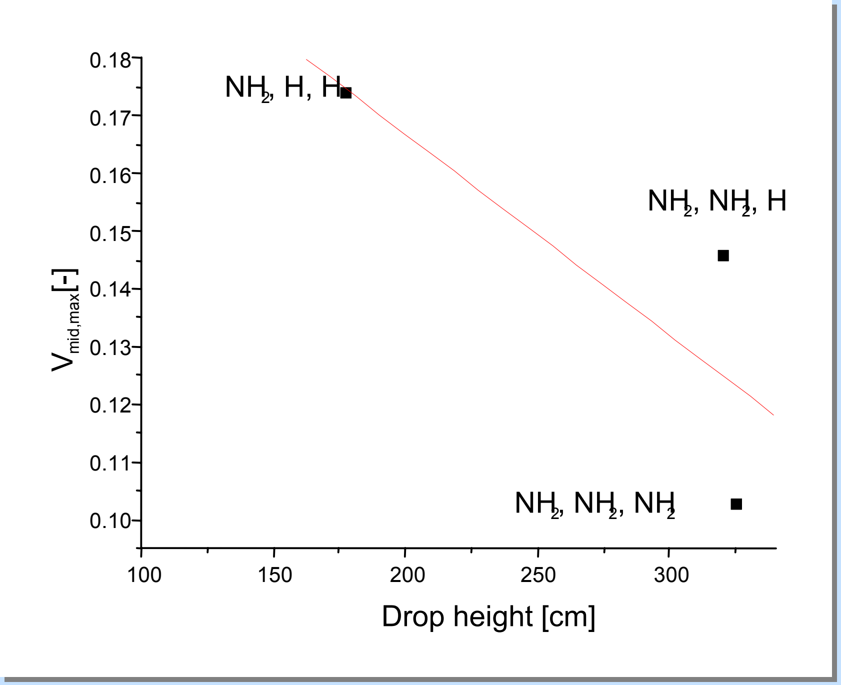
Thus describing and predicting the sensitivity should be based on parameters av[illegible] from simple quantum chemical calculations or even chemical reference monographs.

Impact sensitivity (II)

1,3,5-Trinitrohydroxybenzenes



1,3,5-Trinitroaminobenzenes



Politzer, 1990

As can be seen $V_{mid,max}$ as an indicator of sensitivity is applicable only within very narrow ranges of substituents.

Hence *Politzer* in more recent publications has introduced a series of empirically derived correction terms to allow for a better description of the corresponding systems.

Impact Sensitivity (III)

The „stability“ of a compound according to *Pearson* and *Ho (1977)* can be described via the ratio of the relative hardness values η of the components of a corresponding, hypothetical acid-base-pair. In this context ***ΔN*** can be used as measure for the electronic energy surplus upon formation of such a compound.

Hypothesis:
Stable, impact-insensitive Compounds should possess comparable hardness parameters for the corresponding acid-base pairs. In other words ***ΔN*** should be large for such compounds.

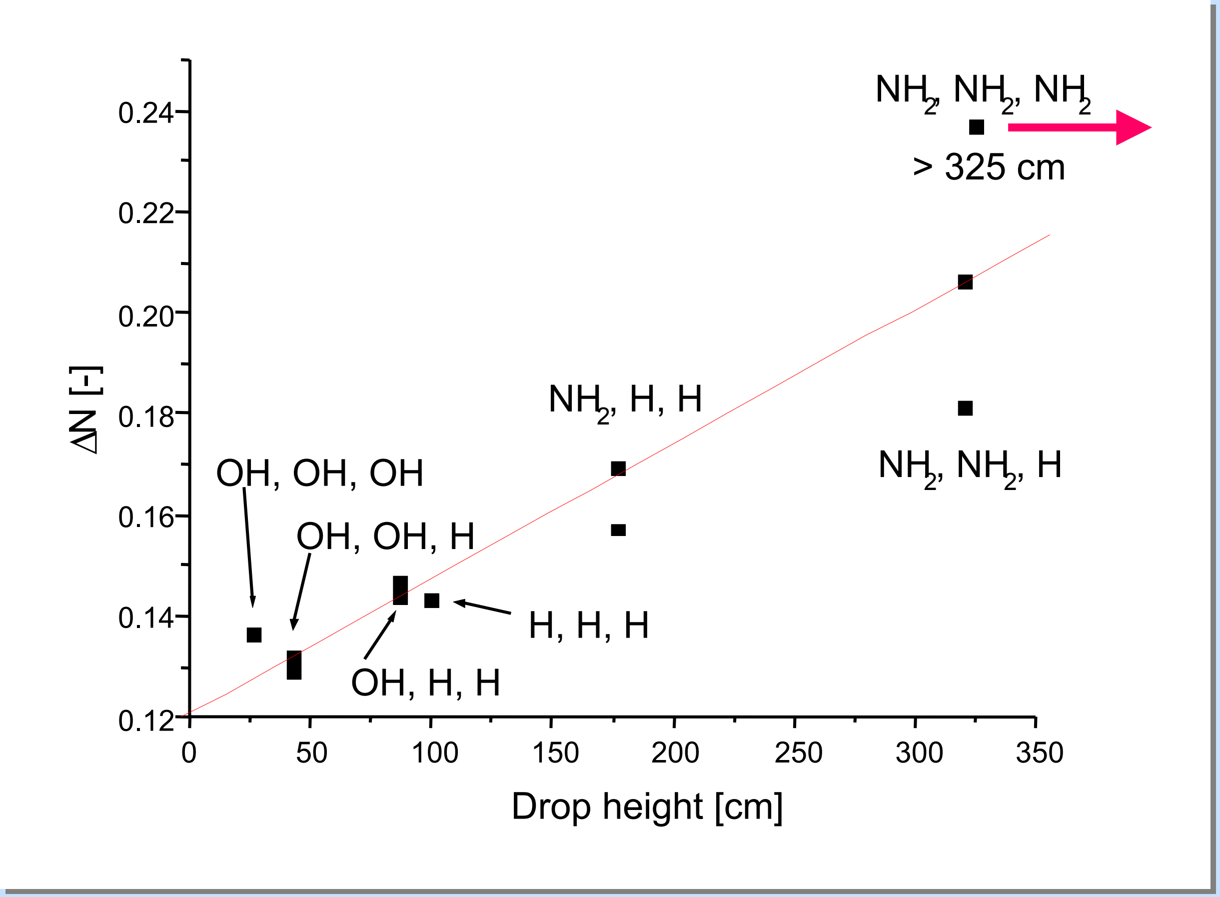
For the corresponding Acid /Base-Pairs(NO_2 / $\bullet C_6R_5$) the HSAB-Parameters χ and η have been calculated on a semiempirical basis (PM3). ΔN has been calculated as described before.

$$R_3C-NO_2 \xrightarrow{impact,shock} R_3C\bullet+\bullet NO_2$$

$$\Delta N=\frac{\chi_{NO_2}-\chi_{C_6R_2(NO_2)_2}}{2\cdot\left(\eta_{NO_2}+\eta_{C_6R_2(NO_2)_2}\right)}$$

Impact sensitivity (IV)

1,3,5-Trinitrobenzene - Derivates



Result:
There is a linear relation between ΔN and the impact sensitivity of 1,3,5-trinitrobenzene derivates

Conclusion

HSAB-parameters help to predict and explain the properties of energetic materials and systems

- A prediction of the relative rates of reaction of binary systems is possible. The example of Mg/PTFE and Mg/PMF shows the applicability of this concept.

- Among aromatic nitro compounds there can be seen a linear relationship between ΔN and dh_{50}.

Outlook

Need for further investigation:

- Investigation of the applicability of ΔN to the performance of other energetic systems such as : metal / nitrate, metal / perchlorate asf.

- Investigation of the applicability of ΔN on the sensitivity of other homogeneous energetic materials, such as aliphatic nitro ($R\text{-}NO_2$) compounds, nitrate esters ($R\text{-}O\text{-}NO_2$)and nitramines ($R\text{-}N\text{-}NO_2$) asf.

References

- R. G. Parr, R. G. Pearson, „Absolute Hardness: Companion Parameter to Absolute Electronegativity“, *J. Am. Chem. Soc.* **1983**, *105*, 7512-7516.
- R. G. Pearson, „Chemical Hardness and Bond Dissociation Energies“, *J. Am. Chem. Soc.* **1988**, *110*, 7684-7690.
- R. G. Pearson, „ Absolute Electronegativity and Hardness: Application to Inorganic Chemistry“, *Inorg. Chem.* **1988**, *27*, 734-740.
- R. G. Pearson, „Absolute Electronegativity and Hardness: Applications to Organic Chemistry“, *J. Org. Chem.* **1989**, *54*, 1423-1430.
- R. G. Pearson, „Chemical hardness and the electronic potential“, *Inorganica Chimica Acta* **1992**, *198-200*, 781-786.
- E.-C. Koch, „ Metal Fluorocarbon Pyrolants: V. Theoretical Evaluation of the Combustion Performance of Metal/Fluorocarbon Pyrolants based on Strained Fluorocarbons“, *Propellants. Explos. Pyrotech.* **2004**, *29*, 9 – 18.
- J. S. Murray, P. Lane, P. Politzer, P. R. Bolduc, „A relationship between impact sensitivity and the electrostatic potentials at the midpoints of $C\text{-}NO_2$ Bonds in Nitroaromatics“, *Chem. Phys. Lett.* **1990**, *168*, 135-139.
- S. R. Davis, „Ab-initio study of the Insertion Reaction of Mg into the Carbon-halogen Bond of Fluoro- and Chloromethane“, *J. Am. Chem. Soc.* **1991**, *113*, 4145-4150.
- L. Liu, S. R. Davis, „Ab-initio-study of the Grignard Reaction between Magnesium Atoms and Fluoroethylene and Chloroethylene“, *J. Phys. Chem.* **1991**, *95*, 8619-8625.
- S. R. Davis, L. Liu, „Ab-initio-study of the insertion reaction of Mg into a C-F-bond of tetrafluoroethylene“, *J. Mol. Struct.* **1994**, *304*, 227-232.
- R. Taylor, J. J. Holloway, E.G. Hope, A. G. Avent, G. J. Langley, J. T. Dennis, J. P. Hare, H.W. Kroto, D. R. M. Walton, „Nucleophilic Substitution of Fluorinated C_{60}“, *J. Chem. Soc., Chem. Commun.* **1992**, 665-667.

Metal Monochloride Emitters in Pyrotechnic Flames — Ions or Neutrals?

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ABSTRACT

Twelve English-language books on pyrotechnics were surveyed for the authors' views on the nature of the metal monochlorides that are associated with the emission of colored light in pyrotechnic flames. Three of the ten authors stated that the emitters were metal chloride ions (MCl^+), five that they were neutral metal chloride molecules (MCl), and two took no clear position. A study of the references cited in these books establishes that the emitters are neutral monochlorides. The idea that they are MCl^+ ions is traced to a book published in 1965, which cited only one reference (published in 1949), and that reference clearly stated that the emitters are neutral molecules.

Keywords: colored flame, emitter, spectra, monochloride, ion, neutral

Introduction

A survey of 12 English-language books on pyrotechnics published since the early 1960s revealed a difference of opinion as to the nature of the metal-chlorine species that contribute to the colours of pyrotechnic flames containing chlorine (Cl) and barium (Ba), calcium (Ca), copper (Cu), or strontium (Sr). Some authors stated that the emitters are neutral monochlorides, MCl, while others indicated that the emitters are singly-charged positive monochloride ions, MCl^+. This review traces the development of this difference of opinion and attempts to establish which of the two points of view is correct by analyzing the information in the references cited in the books. Accordingly, this review has three main parts. It begins with a summary of the positions presented in the 12 books, followed by a summary of the information contained in the references cited in those books. Finally, there is a discussion of that information and of some additional material from more recent publications.

Results of the Book Survey

The following quotes show what each author wrote:

1. Ellern 1961[1]

"Except for the line spectra of the substances usable for colored lights, there is very little literature available on the theoretical aspects and quantitative relations of colored flames. Dr D. Hart [2] refers to the red flame as due to molecular bands in the red region, caused by molecular strontium oxide and chloride, and diluted with other lines and bands from incandescent particles. He refers to the green flame as being due to bright blue (*sic*) bands from copper and barium chloride in the 4000 to 5000 and 5000 to 5500 angstrom region." (p 81)

"Barrow and Caldin [3] have measured the luminous intensities of flare compositions at constant temperature". (p 98)

2. Shidlovskiy 1964 (English translation 1974)[4]

"At high temperatures, strontium chloride dissociates, forming strontium monochloride and splitting off free chlorine:

$2\ SrCl_2 \leftrightarrow 2\ SrCl + Cl_2$" (p 182)

"In practice, red flare compositions are formulated only on the basis of the emission of strontium oxide or strontium monochloride, the emission of the latter being more intense, and in addition, closer to the extreme red portion of the spectrum. This accounts for the effort to introduce chlorine into all the formulations of red flare compositions." (p 183)

"Barium chloride dissociates in a flame, forming barium monochloride and splitting off free chlorine:

$2\,BaCl_2 \leftrightarrow 2\,BaCl + Cl_2$" (p 184)

"The emission spectrum of BaCl consists of numerous bands in the green portion of the spectrum." (p 185)

"The production…of an adequate, pure green flame can be achieved in practice only by using the emission of barium monochloride. Hence, compounds containing chlorine must of necessity be introduced into green flare compositions." (p 185)

"Blue flames are obtained mostly on the basis of cuprous chloride CuCl…The blue emission of cuprous chloride can be obtained only in the reducing zone of the flame and at temperatures not in excess of 1000-1200 °C." (p 186)

"A description of the formulas and technology of German signal-flare compositions used during World War II is given by Eppig.[5]" (p 186)

3. Cackett 1965[6]

"Spectra of illuminating and coloured signal flames are composed of three distinct elements. There is a general temperature continuum derived from the thermal excitation of solid and gaseous products of combustion and which is the main source of the white light that is always present. Next, there are complex systems of band spectra derived from molecular emitters such as ionized oxides and chlorides" (p 30)

"Blue flames rely for their colour on the band-system of $CuCl^+$ ranging from 4200 Å to 4600 Å and to weaker systems in the blue-green and green regions which are simultaneously developed" (p 32)

"All red signal compositions rely on the formation of $SrCl^+$ and SrO^+ ions in the flame to produce their characteristic spectral bands. In practice attention is focussed on developing the $SrCl^+$ ions to a maximum as the SrO^+ ions are always present in the flames." (p 53)

"Green signal compositions, that have really good green flames, are difficult to produce because of the unsaturated hue which is the result of diluting the $BaCl^+$ spectral band with white temperature-continuum and with orange and red spectral bands from BaO^+ and from strontium salts as impurities." (p 56).

4. Ellern 1968[7]

"Color in a flame, as used in pyrotechnics, results from the spectra of excited gaseous metal atoms, molecules or ions [8,9]. Salts of a certain limited number of metals are vaporized and the gaseous molecules or their first partial dissociation products lead to band spectra. On further splitting to neutral atoms of the metal, atomic lines are produced, and eventually metal ions create ionic spectral lines. The latter are undesirable for color production in the flame. So-called C-type chemiluminescence, wherein a small number of molecules emit an abnormally large amount of radiation, plays an important part in the colored emission of red or green flares. An excellent discussion of the mechanisms of pyrotechnic color production is found in reports by Douda.[10,11,12]" (p 97).

5. Lancaster 1972,[13] 1992,[14] and 1998[15]

"Strontium monochloride, barium monochloride and cuprous chloride are the three compounds required for the color production and the excess of chlorine has to be present to ensure their formation".[13] (p 60)

This statement was repeated in the two subsequent editions of this book.[14,15]

6. McLain 1980[16]

"Green flares derive their color from the $BaCl_2$ emission band. As the temperature rises, the BaO^+ emission band increasingly contributes colors in the orange-to-red portion of the spectrum" (p 89)

"Blue is the most difficult color to achieve and bleaches severely when intensity is raised. The blue color comes from the $CuCl^+$ emission band." (p 89)

7. Shimizu 1981[17]

"The important emitters of firework flames are molecules with the exception of Na atoms. The molecules are produced in quite different forms from the original colour producing materials mixed into the composition. The chemical combination of the emitters are relatively simple and in general are outside the ordinary valency law. For example, they are written as SrCl, BaCl, CuCl, etc. and not $SrCl_2$, $BaCl_2$, $CuCl_2$ etc."(p 57)

Pages 59–61 show flame spectra of Sr, Ba, Ca and Cu with and without Cl_2 or HCl. Atomic lines and molecular bands are identified. Figure 47 on page 63 shows the relevant molecular emission bands in relation to the CIE chromaticity diagram.

8. Shimizu 1974[18] (English translation 1983)[19]

"Strontium spectra:

"Strontium salts (carbonate, nitrate, oxalate, etc.) yield the strontium line (4607 Å)…, the SrOH band (5995–6130 Å)…, and the SrCl band (α = 6170–6230Å; β = 6270–6350Å; γ = 6400–6460Å)". (p 75)

"The strontium line is a fairly intense purple-blue. The SrOH band is an intense red-orange, and it is very important for a red colored flame. Chlorine or hydrogen chloride in the flame lowers the intensity of the SrOH band, because the molecule SrOH is changed into SrCl. The α and β bands in the SrCl band are bright red and are the most important components of a good red flame. The γ band is very weak and not important. Chlorine or hydrogen chloride in the flame strengthens the SrCl band. Generally hydrogen chloride has a greater effect than chlorine. If the flame has no chlorine or hydrogen chloride, there will be no SrCl band." (p 76)

"Barium spectra:

"Barium salts (carbonate, nitrate, oxalate, chloride etc.) give the following: barium lines at 5535.5 Å (weak yellow-green), 5778 Å (very weak yellow), and 6100 Å (weak orange)…; BaO band at 4854–6330 Å (very complicated shape, ranging from greenish-blue to red); and the BaCl band at 5505 Å to about 5350 Å (deep green). There are three intense bands: α (5110–5150 Å), β(5245–5280 Å) and γ (5305–5330 Å) …The barium lines are so weak that they have hardly any effect on the flame color. The BaO band is the most important white light source for illumination. It is reduced by the presence of chlorine or hydrogen chloride in the flame, by changing BaO into BaCl. The BaCl band is the most important green light source, but it is only present if chlorine or hydrogen chloride are in the flame. As with strontium, the effect of hydrogen chloride is greater than that of chlorine." (p 76)

"Copper Spectra

"Copper salts (sulfate, arsenite, Paris green, etc.) and powdered copper metal give a purple-blue band (4026–4058,4071–4105, 4123–4164, 4201–4219, 4229–4252, 4269–4277, 4290–4323*, 4340–4343, 4355–4399*, 4417–4432, 4438–4481*, 4496–4513, 4526–4560* Å. … There is also a band from blue to yellow-green (4590–4608, 4630–4658, 4678–4698, 4724–4747, 4769–4781, 4801–4838, 4850–4863, 4888–4928, 4950–4966, 4989–5037, 5056–5074, 5092–5120, 5151–5169, 5190–5225, 5263–5304,5285–5429, 5503–5531, and 5628 Å ...). There is another band at 5263–5531 Å.… The group of purple-blue bands is the most important factor in the production of a blue flame. The asterisks (*) denote the most intense bands. The group of bands from blue to yellow-green is very weak and unimportant. These two groups comprise the CuCl band and become very clear when chlorine or hydrogen chloride are in the flame. The CuCl band appears weaker at temperatures of 2500 °K (2227 °C) and higher because of the decomposition of the CuCl molecule. The other band (5263–5531 Å) comes from CuOH molecules. This is visible when there is no excess chlorine or hydrogen chloride in the flame, and it appears as a weak green color, detracting from a blue flame. Generally our blue flames had a red tip. This is attributable to the copper atom or CuO … the red emissions are very weak and not noteworthy." (p 76)

"Calcium spectra

"Calcium salts such as calcium carbonate give a CaOH band and a CaCl band. The CaOH band… has two portions: an intense red (6105–6270 Å) and intense yellow-green (5500–5580 Å). The CaCl band has four parts: weak red (6294–6360 Å), intense red-orange (6030–6078 Å), intense orange (5915–5986 Å), and slightly weak yellow (5803–5838 Å). The CaOH band occurs in flames in which no chlorine or hydrogen chloride is present. It is not used by itself for producing colored flames. The CaCl band is used as an orange light source. Chlorine or hydrogen chloride intensify the CaCl bands." (p 77)

These quotes were taken from Chapter 7, which consists of 40 pages entirely devoted to colored flames. There are 4 pages of flame spectra. Figure 49 on page 823 shows the relevant molecular emission bands in relation to the CIE chromaticity diagram.

9. Conkling 1985[20]

"The best flame emission in the red region of the visible spectrum is produced by molecular strontium monochloride, SrCl…The SrCl molecule emits a series of bands in the 620–640 nanometer region – the "deep red" portion of the visible spectrum… Strontium monohydroxide, is another substantial emitter in the red and orange-red regions[10,17]. The emission spectrum of a red flare is shown in Figure 7.1…the primary emitting species are SrCl and SrOH molecules in the vapor state".[21]

"Pyrotechnic compositions containing a barium compound and a good chlorine source can generate barium monochloride, BaCl, in the flame and the emission of green light will be observed. BaCl –an unstable species at room temperature –is an excellent emitter in the 505–535 nanometer region of the visible spectrum –the 'deep green' portion [10,17] ... The emission spectrum of a green flare was shown in Figure 4.1 … molecular BaCl in the vapor state, typically the primary emitter of green light".[21]

"The best flame emission in the blue region of the visible spectrum (435-480 nanometers) is obtained from copper monochloride, CuCl. Flame emission from this molecular species yields a series of bands in the region from 428–452 nanometers, with additional peaks between 476-488 nanometers.[10,17]"

10. Akhavan 1998[22]

"Red light is produced by adding strontium compounds to the pyrotechnic mixture. At high temperatures the strontium compound breaks apart and reacts with the chlorine from the oxidizer [i.e. perchlorate (ClO_4^-) molecule] to form $SrCl^+$ as shown in Reaction 8.1.

$$KClO_4 \rightarrow KCl + 2O_2$$

$$KCl \rightarrow K^+ + Cl^-$$

$$Cl^- + Sr^{2+} \rightarrow SrCl^+$$

"It is the $SrCl^+$ molecule which emits light in the red region of the electromagnetic spectrum, ie. 600–690 nm. Green light is produced by adding barium compounds to the pyrotechnic mixture. Green light is emitted from the $BaCl^+$ molecule at 505-535 nm. Blue light is achieved by reacting copper compounds with potassium perchlorate to form $CuCl^+$ which emits light in the blue region of the visible electromagnetic spectrum, ie. 420–460 nm". (p 156)

11. Russell 2000[23]

"Under the influence of heat, oxidisers such as potassium perchlorate decompose into the chloride and oxygen.… At higher temperatures (>2500 °C) the KCl ionises and the chlorine that is liberated reacts with fragments from barium compounds to form light-emitting species such as BaCl in accordance with…

$$KCl \rightarrow K^+ + Cl^-$$

$$Cl^- + Ba^{2+} \rightarrow BaCl^+$$

The main species responsible for the green color of barium flames is BaCl, while contributions are also made from BaO and BaOH as shown in Table 8.1." (p.70)

(This table, on page 71, shows Ba, Ba^+, BaOH, BaO, and BaCl).

"Reference to Table 8.1 shows that in the absence of chlorine-containing species the visible emission is dominated by BaOH, in spite of the fact that the equilibrium concentration of BaOH is many orders of magnitude smaller than that of BaO. The reason for this is that the hydroxide is formed directly in an excited state in a process know as chemiluminescence, as shown by reaction…

$$Ba + OH \rightarrow [BaOH]^* \rightarrow BaOH + h\nu$$

"Here, [BaOH]* is the excited molecule that releases energy … that corresponds to the green region of the visible spectrum." (p 72)

"Strontium chloride has a melting point of 870 °C and exerts a considerable vapour pressure above this temperature. The boiling point of $SrCl_2$ is 1250 °C and at temperatures above this it dissociates forming strontium monochloride and chlorine…

$$2\ SrCl_2 \leftrightarrow 2\ SrCl + Cl_2$$

"At still higher temperatures (the following) reaction …predominates:

$$2\ SrCl + O_2 \leftrightarrow 2\ SrO + Cl_2$$

"An excess of chlorine... causes a shift to the left and an improvement in the flame saturation of strontium monochloride. Table 8.3 shows the main emission bands/lines for a red star." (p 73)

(This Table, on page 73, shows Sr, SrOH, SrCl, and SrO.)

"The main species responsible for the blue colour in copper flames is cuprous chloride, CuCl… In order to produce a good blue, the temperature must be controlled to ensure that the largest possible amount of vaporised CuCl is present in the flame. A typical spectrum shows wavelength peaks in the region 420–500 nm attributable to CuCl band spectra, a peak at 770 nm due to atomic potassium from the oxidizer, together with CuOH band spectra between 535 and 555 nm." (pp 84–85).

12. Hardt 2001[24]

"Many ionized species exist in the gaseous phase as bi- and tri-atomic molecules which give off molecular band spectra that arise from the ability of the molecule to absorb vibrational and rotational energy. Because molecules have fixed masses, sizes and interatomic spacing their rotational and vibrational energies are also quantized and so can take up and emit energies in discrete wavelengths. To the extent that these band spectra are in the visible range, they are of interest to pyrotechnics… The molecular species that give the best colours are the halides of the alkaline earths and copper" (p 40)

Table 6-2 (p 41) lists a number of metal monohalides, monoxides and monohydroxides and the wavelengths of some of their visible emission bands. All are neutral. The reference is to Herzberg.[25]

Summary of the Book Survey

The "neutral molecules" opinion is taught by Ellern[1,7], Shidlovskiy[4], Lancaster[13,14,15], Shimizu[17,19] and Conkling.[20] The "ions" opinion is taught by Cackett[6] and Akhavan.[22] McLain[16] teaches "ions", but also says that green flames are coloured by the emission band of neutral barium dichloride. Russell[23] teaches "neutral molecules", but gives an equation for the formation of BaCl that shows the formation of $BaCl^+$, as if there were no difference. Hardt[24] specifically refers to emitters as "ionized species (that) exist in the gaseous phase as bi- and triatomic molecules", but presents a table of emitters that consists entirely of neutral molecules.

Several authors mention the contribution of metal monohydroxides and monoxides to flame colours; this is clearly an important issue in any discussion of coloured flames. It will not be pursued here, however, because it is not relevant to the question of whether or not the metal chloride emitters are ions or neutrals.

References Cited by the Authors of the Books

1. Ellern 1961[1]

Ellern cited two references that are relevant to the present subject.[2,3]

The writer has not seen the 1953 encyclopedia article by Hart.[2] The 1949 paper by Barrow and Caldin[3] is very much more important than might be guessed from Ellern's remarks. Here is a part of what Barrow and Caldin wrote:

"Blue flames. These rely for their colour on emission of the spectrum of CuCl. Most of the light comes from the D and E systems in the range 4200–4600 Å.[26]; the blue-green systems B and C, and the green system A, are much weaker". (p 33)

"Green flames. BaCl, which gives rise to a well-known band system at 5050–5350 Å, is the obvious choice for a green emitter and it is in fact generally used… The spectrograms of such flames…invariably show the extensive band system of BaO (4000–8000 Å). There is also strong emission from the near infra-red system of BaCl[27] which, however, lies beyond the visible region of the spectrum. Other discrete bands in the region 7000–7600 Å. have not yet been identified." (pp 33–34)

"Red flames. Strontium compounds are used to colour the red flames, but there are still some obscure features in the spectra. The simultaneous presence of strontium and chlorine compounds in the compositions leads to strong emission of the red system of SrCl (the violet system also appears weakly). However there are also present two closely-spaced sequences degraded to the violet which do not belong to the SrCl system. The long wavelength edges of these sequences are at 6884.5 and 6114.2 Å. In strontium flames containing no chlorine these heads are more strongly developed, and, in addition, the region between them can be seen to be filled with a very close pattern of what appear to be rotational structure lines. The most likely emitter would seem to be SrO, and it is some support for this suggestion that a heavy-current positive-column discharge through SrO contained in a silica tube leads to the production of the same bands." (p 34)

Barrow and Caldin, who were academic spectroscopists, clearly teach that the emitters are neutral molecules. The writer has not seen the 1941 edition of Pearse and Gaydon's book[26] that was cited by Barrow and Caldin, but the following quotes from the 1963 edition[28] are highly relevant:

"Without exception, flame bands have been found to belong to molecules which are electrically neutral, but very frequently the molecules are not stable in the chemical sense..." (p 322)

"BaCl Green System

"Occurrence. Barium chloride in carbon arc or flame". (p 77)

"(BaCl) Infra-red System

"Occurrence. In the flame of pyrotechnic compositions." (p 78)

"BaO

"Occurrence. When barium salts are introduced into carbon arc or flame". (p 82)

"BaOH

"The strong green coloration of flames containing barium salts has recently been shown to be due to the triatomic hydroxide, not the oxide." (p 82)

"CuCl

"Occurrence. Five systems have been observed in flames, in fluorescence and in absorption. They also appear when CuCl is introduced into active nitrogen, and in an arc. The bands frequently occur as impurities in flame spectra, especially of CO…The group of pairs of bands formed by systems D and E is quite characteristic. See Plate 10." (p 152)

"SrCl

"Occurrence. When strontium chloride is introduced into an arc or flame". (p 294)

"SrO

"Strontium salts give bright red banded radiation in flames and arcs, but the flame bands are mostly due to SrOH." (p 298)

"SrOH

"These bands are responsible for the strong red colour of flames and fireworks containing strontium." (p 299)

Pearse and Gaydon[28] often give details of the electronic transitions that are associated with the various bands in spectrum of each molecule, with references to the primary spectroscopic literature from the late 1920s to the late 1950s.

Barrow and Caldin's paper,[3] especially when supplemented by the information in Pearse and Gaydon's book[28], provides very strong support for the neutral molecule position and none whatsoever for the ion position.

2. Shidlovskiy 1964 (English translation 1974)[4]

Shidlovskiy did not cite specific reference for his statements on the nature of the flame emitters. The writer has not seen the report on German signal flare compositions[5] mentioned by Shidlovskiy.

3. Cackett 1965[6]

Cackett, who was the first to present the "ion" opinion, cited but one reference in his discussion of coloured flames: Barrow and Caldin.[3] Cackett did not mention that his identification of the emitters as positive metal monochloride ions was at odds with his cited reference, and he offered no justification for his new identification of the emitters.

4. Ellern 1968[7]

The two relevant references cited in Ellern's 1961[1] book are cited again in this book, but in a different context. Hart's encyclopaedia article[2] is mentioned as "an authoritative article on military pyrotechnics" in the section covering the literature of pyrotechnics (p 10) but there is no mention of his views on colour emitters. Barrow and Caldin[3] are cited in the chapter on colored lights in support of the statement that blue signal lights "seem to be somewhat maligned and deprecated, apparently not so much on optical grounds but because it is difficult and perhaps impossible to create a blue pyrotechnic flame of great depth of color." (p 123) The contribution of these authors in identifying the emitters is not mentioned.

Ellern also cited five works by Douda.[8–12] One of these[8] refers to another of Douda's works[10] for a discussion of the theory of coloured flames and one of the others[9] is a patent of no direct relevance to the present subject.

Of the remaining three works by Douda, the first[10] is a monograph covering all aspects of coloured flame production. It includes references to 18 sources, including five that discuss ionization in flames. Douda attributed the red colour of Sr flames to SrCl and SrOH, and the green of Ba flames to BaCl and BaOH. He explained that addition of halogen to the flame is expected to increase the concentration of the metal hydroxide, and he continued: "In both instances, because the pyrotechnic compositions are usually saturated with the metal and halogen, a very substantial amount of the metal halide will be present in the flame in addition to the hydroxide. The halide formation with barium and strontium is not objectionable because these molecules fortunately also emit energy as defined by their molecular band spectrum in the desired wavelength." (p 18).

Referring to flames containing copper, Douda wrote "As in the case of barium and strontium, the halogen combines with hydrogen to form the halide acid, thereby causing an OH excess which, in turn, contributes to the formation of more CuOH, Also, as in the case of barium and strontium, although more metal hydroxide is formed, the metal halide is formed in even greater amounts. Because the strontium and barium halides emit in desirable wavelengths, the net result is a quantitative increase of emission in desirable wavelengths. In the case of copper, however, the increase in CuOH is out weighed by the increase in copper halide formation, thus resulting in a shift from CuOH green emission to blue copper halide emission." (p 22).

The next work of Douda cited by Ellern[7] is a technical report[11] in which Douda wrote: "Strong BaCl emissions have been reported at 524 mμ and for BaOH at 527 mμ." (p 6)

"Strong SrCl and SrOH emissions occur in this region" [i.e., around 640 mμ]. (p 6)

"BaCl and BaOH dominate in green barium flames." (p 6)

"SrCl and SrOH dominate in red strontium flames". (p 6)

The last work of Douda cited by Ellern[7] is a paper[12] on green flares. Douda wrote:

"In the presence of chlorine, the suppression of MgO and BaO flame emission is a decreasing function of effective temperature, and the ratio BaO/BaCl is an increasing function of effective temperature accompanied by a shift of hue toward yellow and a reduction in excitation purity. By analogy with dissociation constants reported for BaF and BaOH, the dissociation energy of BaCl is estimated to be near 100 kcal/mole. Such an increased value more readily accounts for the sizable BaCl emission observed at a brightness temperature of 2200 K and an effective emitting temperature of 2700 K. Evidence concerning the contribution of BaOH is inconclusive. The 107 kcal/mole dissociation energy in comparison with the 100 kcal/mole estimated for BaCl suggests that BaOH should also be a substantial contributor." (p 793)

5. Lancaster 1972,[13] 1992,[14] and 1998[15]

Lancaster did not cite specific references for his statement about colour emitters. His first edition[13] has a list of 23 references including the first (Russian, 1943) edition of Shidlovskiy, both of Ellern's books[1,7] and a 1957 Japanese-language book by Shimizu.[29] The second edition has 40 references, including all of those in the first edition. Relevant additions include both of Shimizu's books discussed above,[17,19] the books by McLain[16] and Conkling,[20] and to *Pyrotechnica*.[30] The third edition of Lancaster's book[15] has 76 references, but none of those added since the second edition appear to be relevant to the present topic.

6. McLain 1980[16]

McLain did not cite specific reference for his statements quoted above. His chapter on "Light" has a list of 14 references including Ellern,[7] Shidlovskiy,[4] Cackett,[6] Lancaster[13] and a work by Douda[31] that deals with the characteristics of the spectra of magnesium-sodium nitrate-binder illuminating flares. McLain adopted the ion teaching of Cackett, despite the opposing views of Ellern, Shidlovskiy, Lancaster and Douda. It is noteworthy that Douda's writings on coloured flames[10,11,12] were not cited by McLain.

7. Shimizu1981[17]

Shimizu did not cite specific reference for his statements quoted above. His book has a list of 13 references including Ellern,[7] Shidlovskiy,[4] Lancaster,[13] and three of his own books.[29,18,32] He also lists *Pyrotechnica* Issues I– IV.[30]

8. Shimizu 1974[18] (English translation 1983)[19]

In this work Shimizu listed 11 references concerning flame spectra. These include Pearse and Gaydon's book,[28] along with 10 references to the primary spectroscopic literature. Many of these refer to oxide and monohydroxide emitters, but four deal specifically with the spectra of neutral metal monohalides.[33-36]

9. Conkling 1985[20]

As indicated above, Conkling cited specific references for his statements. As well as works of Douda[10] and Shimizu[17] that have already been discussed, Conkling cited a 1983 report by Webster.[21] The writer has not seen this report, but Webster published a paper[37] having the same title in 1986 and this presumably contains much the same information. It includes emission spectra of red, green and yellow flares. Webster wrote:

"The primary emitting species in the red flare are SrCl and SrOH. Emission bands from the SrCl $A^2\Pi \rightarrow X^2\Sigma^+$ system are observed at 661.4 nm, 662.0 nm 674.5 nm and 675.6 nm. Emission from the SrCl $B^2\Sigma \rightarrow X^2\Sigma^+$ system is observed at 623.9 nm, and 648.5nm. The band in both these systems show sharp band heads and are degraded to the violet. …Bands from the SrCl $C^2\Pi \rightarrow X^2\Sigma^+$ system were observed at 393.7 nm, 396.1 nm and 400.9 nm. Molecular emission from the SrOH band system (was) observed…at 605.0 nm, 646.0 nm, 659.0 nm, 667.5 nm and 682.0 nm. The bands at 646.0 nm, 659.0 nm and 667.5 nm overlap the SrCl bands at these wavelengths. This makes the SrCl bands appear stronger and more diffuse than would normally be expected." (p 2)

"The primary emitting species in the green flare are BaCl and BaO. Emission bands from the BaCl $C^2\Pi \rightarrow X^2\Sigma^+$ system are observed at 507 nm, 514 nm 524 nm and 532 nm. The molecular BaCl emission is superimposed on less intense, but equally important BaO, BaOH and Ba_2O_2 band emission extending from 460 nm to 678 nm. This emission, coupled with an underlying continuum from hot solid particles, is the contributing factor to the loss of color purity in the flare. The …flare composition also contains copper and the resulting CuCl emissions are observed from 412 nm–470 nm." (p 3) Webster cited the following references: Douda,[12,38] McLain,[16] Shimizu,[17] Barrow and Caldin.[3] and Ellern.[7] All of these have already been discussed, except Douda's 1972 paper[38] on the spectrum of a red highway flare. Douda wrote:

"The dominant emitting species are strontium oxide and the flame radicals SrCl and SrOH, the radicals being strong emitters[39,28] in the red region. The strong band systems with maxima near 606, 646, 659, 669 and 682 nanometers are due mainly to emission from SrOH and SrCl." (pp 416–417) Reference [39] deals with magnesium-metal nitrate flares with no chlorine donors and is only marginally relevant to the present discussion.

10. Akhavan 1998[22]

Akhavan cited no specific references for her statements. Her bibliography includes Conkling[20] and Ellern[7].

11. Russell 2000[23]

Russell cited no specific references for his statements. His bibliography includes Ellern[7], McLain[16] and Lancaster[15].

12. Hardt 2001[24]

Hardt did not cite specific references for his statements, but he cited Hertzberg[25] for the information presented in his Table 6-2. Hardt's bibliography contains over 270 references, up to the year 1999. These include 14 works by Douda but of these only one[10] is clearly relevant to the present topic. Another of the cited works of Douda[40] deals with the emission spectra of flares but is concerned only with magnesium-sodium nitrate-binder illuminating flares.

Evidence That the Metal Monochloride Emitters Are Neutral Molecules, Not Ions

1) The spectra of the neutral metal monochlorides are very well known to spectroscopists. For example, in 1979 Huber and Hertzberg[41] published a volume of spectroscopic constants for all known diatomic molecules and ions, covering the literature up to 1975. They cited 14 references for data on BaCl, 14 for CaCl, 15 for CuCl and 11 for SrCl. More recently an on-line data base of references associated with the spectra of diatomic molecules[42] contained, in January 2004, 36 papers associated with the spectrum of BaCl, 61 for the CaCl spectrum, 50 for the CuCl spectrum, and 19 for the SrCl spectrum. All of these papers have been published since 1974.

2) The Ca, Sr and Ba monochlorides are members of a rather large family of univalent alkaline earth compounds that exist at high temperatures and that have been characterized spectroscopically in recent years.[43] The alkaline earth monohydroxide emitters are members of this same group of compounds.[43]

3) The electronic states of the metal monochlorides have been calculated from quantum mechanics. The predicted spectra are in good agreement with those measured experimentally. See, for example, the comparison of calculated results for the CuCl molecule with experimental results by Parekunnel et al.[44]

4) The number of electrons in an emitter can be determined from the characteristics of the spectrum.[45] Each electron carries half a unit of angular momentum ("spin") that can have one of two directions, corresponding to a spin of plus or minus ½ a unit in some reference direction. If two electrons of opposite spin "pair up", the spins cancel; if an atom or molecule has one or more unpaired electrons, the resulting electron spin interacts with the angular momentum associated with the movement of electrons around the atom or molecule and changes the energy of the electrons. If there is no unpaired electron, the electronic energy state is unaffected by electron spin. Such a state is called a "singlet". If there is a single unpaired electron, its spin can either add to, or subtract from, the component of the angular momentum of the electronic energy states in the reference direction, with the proviso that the resulting angular momentum must always be positive. Consequently, a state having an angular momentum component in the reference direction of 1 unit is split into two, one of the new states having angular momentum of ½ unit and the other 1½ units. Such a state is called a "doublet". Two unpaired electrons result in an electronic energy state splitting into three, called a "triplet". In general, the *multiplicity* of a state is one more than the number of unpaired electrons. If an atom or molecule has an even number of electrons, the multiplicity of all its electronic energy

levels must be odd, and conversely. An obvious example of the effect of multiplicity on an electronic spectrum is provided by the sodium atom, which has a single unpaired electron. The "doublet" nature of the electronic energy states of atomic sodium is revealed by the familiar yellow line in the spectrum of atomic sodium actually consisting of two lines.

The characteristics of molecular spectra that indicate the multiplicity of the emitter are more subtle. The analysis involves careful study of the rotational structure of the various bands and is possible only with spectra recorded at very high resolution. Details are given by Gaydon[46] and by Herzberg.[25,45] Analysis of the spectra of the alkaline earth monochlorides reveals that the electronic energy states are doublets.[28,34,47] This means that there is an odd number of electrons in the emitter, which is the case for the neutral monochloride molecules but not for the ions. Similarly, the spectrum of copper monochloride[44] reveals singlet and triplet states, showing that the emitter has an even number of electrons. This is consistent with the emitter being neutral copper monochloride but not with it being the ion.

5) Thermodynamic modeling of the combustion of coloured flame compositions[48,49] has shown the presence of neutral metal monochlorides in the predicted equilibrium mixture of combustion products, consistent with the observed emission spectra.

6) The ions $CaCl^+$, $SrCl^+$ and $BaCl^+$ would presumably have exactly the same electronic structure as the molecules KCl, RbCl and CsCl respectively. The alkali chlorides do not exhibit visible spectra[25, 41] and it is expected that the same would be true of the alakaline earth monochloride ions.[50] Huber and Herzberg[41] and the DiRef[42] database list no spectroscopic data for $CaCl^+$, $SrCl^+$, $BaCl^+$ or $CuCl^+$, Hildenbrand[51] measured the ionization energies of CaCl, SrCl, BaCl and CuCl by mass spectrometry, using electron impact ionization. Results, expressed as the appearance potential for each MCl^+ ion from the corresponding MCl precursor molecule, are shown in Table 1.

Table 1. Ionization Energies of CaCl, SrCl, BaCl and CuCl.[51]

Ion	Appearance potential (eV)
$CaCl^+$	5.6 ± 0.5
$SrCl^+$	5.3 ± 0.5
$BaCl^+$	5.0 ± 0.5
$CuCl^+$	10.7 ± 0.5

The ionization energy of CuCl is so high that only a very small fraction of any population of CuCl molecules present in a flame could possibly be ionized at flame temperatures. Furthermore, only a tiny fraction of those ions would be excited at flame temperatures. The number of emitting ions at flame temperatures would therefore be exceedingly small. This consideration alone is sufficient to rule out the possibility that $CuCl^+$ could be a significant emitter of light in a pyrotechnic flame.

Conclusion

The metal monochloride spectra that contribute to the colours of pyrotechnic flames are emitted by neutral metal monochloride molecules, MCl where M is Ba, Ca, Cu or Sr. This was clearly stated by Barrow and Caldin[3] as long ago as 1949 and has been confirmed since by Douda,[8–12,39–41] Shimizu,[17–19] and Webster.[21,37,47] The idea that the emitters are singly-charged metal monochloride ions (MCl^+) is erroneous, and can be traced to the 1965 book by Cackett.[6] At the time that Cackett wrote his book, no spectra of the monohalide ions of Ba, Ca, or Sr had been reported in the scientific literature,[41] none have been reported since[42] and there are good reasons for expecting that these ions would not emit visible spectra.[50] Similarly, there are no reports of spectra of $CuCl^+$;[41,42] the high ionization energy of this ion[51] make it most unlikely that it could exist in a flame in sufficient numbers to contribute in any significant way to the emission of light by the flame.

A Note on Nomenclature

The neutral MCl, etc. molecules are referred to herein as “neutrals”. Douda[38] used the term “radicals” for SrCl and SrOH. This terminology was not adopted here, because Herzberg[46] used “radicals” to include all short-lived species, including molecules and ions.

Acknowledgements

I appreciate the interest of the “Ions or Neutrals?” group. This group is a collection of 14 authors and researchers, all having an interest in pyrotechnic flame colour, to whom the paper was submitted for critical comments.

I am grateful to Kenneth L. Kosanke for initiating this project and for supplying copies of many of the papers consulted for this review. Bernard E. Douda very kindly provided copies of some of his papers. I thank Peter F. Bernath for helpful comments and for drawing my attention to the “DiRef” database.[42]

References

1) H. Ellern, *Modern Pyrotechnics*, Chemical Publishing Co., Inc., NY (1961) pp 81, 98.

2) D. Hart, “Pyrotechnics (Military)”, *Encyclopedia of Chemical Technology*, Vol. 11, Interscience Publishers, Inc., NY (1953) (cited by Ellern[1]).

3) R. F. Barrow and E. F. Caldin, “Some Spectroscopic Observations on Pyrotechnic Flames”, *Proceedings of the Physical Society (London)*, 62B, pp 32–39 (1949).

4) A. A. Shidlovskiy, *Principles of Pyrotechnics*, 3rd Ed., Mashinostoyeniye Press, Moscow, 1964, translated by Foreign Technology Division, Wright-Patterson Air Force Base, OH (1974) pp 182–186.

5) H. Eppig, *The Chemical Composition of German Pyrotechnic Colored Signal Lights*, London, 1945 (cited by Shidlovskiy[4]).

6) J. C. Cackett, *Monograph on Pyrotechnic Compositions*, Ministry of Defence (Army), Royal Armament Research and Development Establishment, Fort Halstead, Sevenoaks, Kent, UK, 1965, pp 30, 32, 53, 56. (NOTE: This book is marked “RESTRICTED”. The writer was fortunate enough to find a copy in a secondhand bookshop in Melbourne, Australia in 2003).

7) H. Ellern, *Military and Civilian Pyrotechnics*, Chemical Publishing Co., Inc., NY, 1968, p 97.

8) B. Douda, *Colored Flare Ingredient Synthesis Program*, RDTR No. 43, Naval Ammunition Depot, Crane, IN, 10 Jul 1964.

9) B. Douda, *Pyrotechnic Compound Tris(glycine) Strontium(II) Perchlorate and Method for Making Same,* US Patent 3,296,045, 1967.

10) B. Douda, *Theory of Colored Flame Production*, RDTN No. 71, Naval Ammunition Depot, Crane, IN, 20 Mar 1964.

11) B. Douda, *Relationships Observed in Colored Flames*, RDTR No. 45, Naval Ammunition Depot, Crane, IN, 25 Sep 1964.

12) B. E. Douda, “Emission Studies of Selected Pyrotechnic Flames”, *Journal of the Optical Society of America*, Vol. 55, No. 7 (1965) pp 787–793.

13) R. Lancaster, T. Shimizu, R.E.A. Butler and R.G. Hall, *Fireworks Principles and Practice*, Chemical Publishing Co., NY, 1972, p 60.

14) R. Lancaster, with contributions from T. Shimizu, R.E.A. Butler and R.G. Hall, *Fireworks Principles and Practice*, 2nd ed., Chemical Publishing Co., NY, 1992, p 77.

15) R. Lancaster, with contributions from R.E.A. Butler, J. M. Lancaster, T. Shimizu and T. A. K. Smith, *Fireworks Principles and Practice*, 3rd ed., Chemical Publishing Co., NY, 1998, p 142.

16) J. H. McLain, *Pyrotechnics from the Viewpoint of Solid State Chemistry*, The Franklin Institute Press, Philadelphia, 1980, p 89.

17) T. Shimizu, *Fireworks – The Art, Science and Technique*, published by T. Shimizu, distributed by Maruzen Co., Tokyo, 1981, pp 57–63.

18) T. Shimizu, *Feuerwerk von physikalischem Standpunkt aus,* Hower Verlag, Hamburg, 1976. (Cited by Shimizu[17] – see reference 19 for English translation).

19) T. Shimizu, *Fireworks from a Physical Standpoint*, translated from the German *Feuerwerk von physikalischem Standpunkt aus*, 1976, by Alex Schuman, Pyrotechnica Publications, Austin, TX, 1983. Part II, p 74–83, Part IV, p 246.

20) J. A. Conkling, *Chemistry of Pyrotechnics*, Marcel Dekker, NY, 1985, pp 87, 157, 158, 160.

21) H. A. Webster III, "Visible Spectra of Standard Navy Colored Flares", *Proceedings, Explosives and Pyrotechnics Applications Section, American Defense Preparedness Association*, Fort Worth, TX, Sep 1983.

22) J. Akhavan, *The Chemistry of Explosives*, Royal Society of Chemistry, Cambridge, 1998, p 156.

23) M. S. Russell, *The Chemistry of Fireworks*, Royal Society of Chemistry, Cambridge, 2000, pp 70–74, 84–85.

24) A. P. Hardt, with contributions by B. L. Bush and B. T. Neyer, *Pyrotechnics*, Pyrotechnica Publications, Post Falls, ID, 2001, pp 40–41.

25) G. Herzberg, with the cooperation, in the first edition, of J. W. T. Spinks, *Molecular Spectra and Molecular Structure. Vol. I. Spectra of Diatomic Molecules*, 2nd ed., D. Van Nostrand, Inc., Princeton, NJ, 1950, pp 240–280.

26) R. W. B. Pearse and A. G. Gaydon, *The Identification of Molecular Spectra* , Chapman and Hall, London, 1941. (Cited by Barrow and Caldin.[3])

27) R. F. Barrow and D. V. Crawford, "Electronic Band System of BaCl", *Nature*, Vol. 157 (1946) p 339.

28) R. W. B. Pearse and A. G. Gaydon, *The Identification of Molecular Spectra*, Chapman and Hall, London, 1963.

29) T. Shimizu, *Hanabi*, Hitotsubashi Shobo, Tokyo, 1957. (Cited by Lancaster[14,15] and Shimizu.[17])

30) R. G. Cardwell, Ed., *Pyrotechnica*, Vol. I – Vol. XVII, Pyrotechnica Publications, Austin, TX (1977–1997).

31) B. E. Douda, "Spectral Observations in Illuminating Flames", RDTR No. 131, in *Proceedings of the First Pyrotechnic Seminar*, U.S. Naval Ammunition Depot, Crane, IN, October 1968, pp 113–125.

32) T. Shimizu, *Hanabi no Hanashi*, Kawada Shobo Shisha, Tokyo, 1976. (Cited by Shimizu.[17])

33) R. Ritschl, "Uber den Bau einer Klasse von Absorptionsspektren", *Zeitschrift fur Physik*, Vol. 42 (1927) pp172–210.

34) A. E. Parker, "Band Systems of BaCl", *Physical Review*, Vol. 46 (1934) pp 301–307.

35) R. R. Rao and J. K. Brody, "Structure of the Band Spectra of CuCl Molecule, I. Additional Knowledge in the Coarse Structure", *Journal of Chemical Physics*, Vol. 35 (1961) pp 776–787.

36) R. R. Rao, R. K. Asundi and J. K. Brody, "Structure of the Band Spectra of CuCl Molecule, II. Rotational Structure of the F-X Band System of CuCl, *Canadian Journal of Physics*, Vol. 40 (1962) pp 412–422.

37) H. A. Webster, III, "Visible Spectra of Standard Navy Colored Flares", *Propellants, Explosives, Pyrotechnics*, Vol. 10 (1985) pp 1–4.

38) B. E. Douda "Red Highway Flare Spectrum", *American Journal of Optometry and Archives of American Academy of Optometry*,Vol. 49, No. 5 (1972) pp 415–417.

39) B. E. Douda, R. M. Blunt, and E. J. Bair, "Visible Radiation from Illuminating-Flare Flames: Strong Emission Features", *Journal of the Optical Society of America*, Vol. 60, No. 8 (1970) pp 1116–1119.

40) B. E. Douda, *Atlas of Radiant Power Spectra of Four Flare Formulations at 8 Levels of Atmospheric Pressure*, RDTR No. 205,

Naval Ammunition Depot, Crane, Inn June 1972.

41) K. P. Huber and G. Herzberg*, Molecular Spectra and Molecular Structure, Vol. IV. Constants of Diatomic Molecules*, Van Nostrand Reinhold, NY, 1979.

42) P.F. Bernath and S. McLeod, "DiRef, A Database of References Associated with the Spectra of Diatomic Molecules", *Journal of Molecular Spectroscopy*, Vol. 207, (2001) p 287.

43) P. F. Bernath, "Gas-phase Inorganic Chemistry: Monovalent Derivatives of Calcium and Strontium", *Science*, New Series, 254 (issue 5032) (1991) pp 665–670.

44) T. Parekunnel, L. C. O'Brien, T. L. Kellerman, T. Hirao, M. Elahine and P. F. Bernath, "Fourier Transform Emission Spectroscopy of CuCl", *Journal of Molecular Spectroscopy*, Vol. 206 (2001) pp 27–32.

45) G. Herzberg, *The Spectra and Structure of Simple Free Radicals: An Introduction to Molecular Spectroscopy*, Dover Publications, NY, 1971, pp 74–88.

46) A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules*, Chapman and Hall, London (1947) pp 25–26.

47) A. E. Parker, "Band Systems of MgCl, CaCl and SrCl", *Physical Review*, Vol. 47 (1935) pp 349–358.

48) R. E. Farren, R. G. Shortridge and H. A. Webster, III, 'Use of Chemical Equilibrium Calculations to Simulate the Combustion of Various Pyrotechnic Compositions", *Proceedings of the 11th International Pyrotechnics Seminar*, 1986, pp 13–40.

49) R. Webb and M. van Rooijen, "Optimizing Pyrotechnic Color Compositions using Thermodynamic Modeling", *Proceedings of the 29th International Pyrotechnics Seminar*, 2002, pp 823–828.

50) P. F. Bernath, personal communication, January 2004.

51) D. L. Hildenbrand, "Dissociation Energies and Chemical Bonding in the Alkaline-Earth Chlorides from Mass Spectrometric Studies", *Journal of Chemical Physics*, Vol. 52 (1970) pp 5751–5759.

Metal Monochloride Emitters in Pyrotechnic Flames – IONS or NEUTRALS

Barry Sturman
Journal of Pyrotechnics
Issue 19, 2004, pp 1-13

Summarized by: Ken Kosanke

Background to Paper

- **About 1-1/2 years ago Rutger Webb raised the question as to:**
  - **Why there were two schools of thought regarding the nature (ions or neutrals) of the color emitting species in pyrotechnic flames?**
  - **Which group was correct?**

Background to Paper

- I assembled a group of individuals (from both schools of thought) to discuss the issue:

**Jacqueline Akhavan, Tony Cardell,
John Conkling, Nigel Davies, Dan Dolata,
Bernie Douda, Brian Ingram, Ernst Koch,
Ron Lancaster, Roy Lowry,
Will Meyerriecks, Darren Naud,
Barry Sturman, and Rutger Webb**

Background to Paper

- To facilitate the discussion, it was immediately apparent that a comprehensive summary of the literature on the subject was needed.

- Barry Sturman agreed to take on that major task, which was intended to end up as a paper for the *Journal of Pyrotechnics*.

Background to Paper

- Barry did this by:
  - First consulting 12 books that addressed pyrotechnic flame color production.

Ellern (1961), Shidlovskiy (1964), Cackett (1965),

Ellern (1968), Lancaster (1972, 1992, 1998),

Shimizu (1974), McLain (1980), Shimizu (1981),

Conkling (1985), Akhavan (1998), Russell (2000),

and Hardt (2001)

Background to Paper

- **Barry did this by:** (continued)
  - **Then consulting the references cited by the authors of the books, and in some cases by consulting secondary references cited by the primary references. (approximately 40 references in total).**
- **In the course of this work, Barry was able to expand his scope to address how the two schools came about and which was almost certainly correct.**

Background to Paper

- Over the course of Barry’s work, the discussion group was offered a chance to contribute their initial thoughts, and they were supplied the rough and final drafts of his paper.
- The members of the discussion group were then encouraged to comment on Barry’s paper, especially if they were not in agreement with his conclusions.

Summary of Barry's Paper

- **Why not present the full paper here?**
  - **It is too long and much too detailed to be easily digested as a seminar.**

- **If you want the full paper:**
  - **It is in the *Workshop Proceedings*, or Bonnie Kosanke has brought a few copies of the *Journal of Pyrotechnics* with the article.**

Summary of Barry's Paper

- **The "neutral molecules" opinion is taught by book authors Ellern,**[1,7] **Shidlovskiy,**[4] **Lancaster,**[13–15] **Shimizu,**[17,19] **and Conkling.**[20]
- **The "ions" opinion is taught by book authors Cackett**[6] **and Akhavan.**[22]

Summary of Barry's Paper

- Cackett, who was the first to present the "ion" opinion, cited but one reference in his discussion of coloured flames: Barrow and Caldin.[3]
  - Cackett did not mention that his identification of the emitters as positive metal monochloride ions was at odds with his cited reference, and
  - he offered no justification for his new identification of the emitters.

Summary of Barry's Paper

- **Akhavan cited no specific references for her statements. However her bibliography included book authors Conkling[20] and Ellern.[7]**

Summary of Barry's Paper

- **Book author McLain[16] teaches "ions", but also says that green flames are coloured by the emission band of neutral barium dichloride.**

- **Book author Russell[23] teaches "neutral molecules", but gives an equation for the formation of BaCl that shows the formation of BaCl+, as if there were no difference.**

Summary of Barry's Paper

- **Book author Hardt[24] specifically refers to emitters as "ionized species (that) exist in the gaseous phase as bi- and tri-atomic molecules", but presents a table of emitters that consists entirely of neutral molecules.**

Evidence That the Emitters Are Neutral Molecules, Not Ions.

- **1) The spectra of the neutral metal monochlorides are very well known to spectroscopists. For example, ….**

- **2) The Ca, Sr and Ba monochlorides are members of a rather large family of univalent alkaline earth compounds that exist at high temperatures and that have been characterized spectroscopically in recent years.**[43] **….**

Evidence That the Emitters Are Neutral Molecules, Not Ions.

- **3) The electronic states of the metal monochlorides have been calculated from quantum mechanics. The predicted spectra are in good agreement with those measured experimentally. See, for example, ….**

Evidence That the Emitters Are Neutral Molecules, Not Ions.

- **4) The number of electrons in an emitter can be determined from the characteristics of the spectrum.**[45] **….**
  - **If there is no unpaired electron, the electronic energy state is unaffected by electron spin. Such a state is called a “singlet”.** (Continued)

Evidence That the Emitters Are Neutral Molecules, Not Ions.

- **4) (Continued)**
  - **If there is a single unpaired electron, its spin can either add to, or subtract from, the component of the angular momentum of the electronic energy states in the reference direction, …. Such a state is called a “doublet”.** (Continued)

Evidence That the Emitters Are Neutral Molecules, Not Ions.

- **4) (Continued)**
  - **Two unpaired electrons result in an electronic energy state splitting into three, called a "triplet".**
  - **In general, the *multiplicity* of a state is one more than the number of unpaired electrons. ….**(Continued)

Evidence That the Emitters Are Neutral Molecules, Not Ions.

- **4) (Continued)**
  - **Analysis of the spectra of the alkaline earth monochlorides reveals that the electronic energy states are doublets.** [28,34,47] **This means that there is an odd number of electrons in the emitter, which is the case for the neutral monochloride molecules but not for the ions.** (Continued)

Evidence That the Emitters Are Neutral Molecules, Not Ions.

- **4) (Continued)**
  - **Similarly, the spectrum of copper mono-chloride[44] reveals singlet and triplet states, showing that the emitter has an even number of electrons. This is consistent with the emitter being neutral copper monochloride but not with it being the ion.**

Evidence That the Emitters Are Neutral Molecules, Not Ions.

- **5) Thermodynamic modeling of the combustion of coloured flame compositions[48,49] has shown the presence of neutral metal mono-chlorides in the predicted equilibrium mixture of combustion products, consistent with the observed emission spectra.**

Evidence That the Emitters Are Neutral Molecules, Not Ions.

- **6) The ions $CaCl^+$, $SrCl^+$ and $BaCl^+$ would presumably have exactly the same electronic structure as the molecules KCl, RbCl and CsCl respectively. The alkali chlorides do not exhibit visible spectra**[25, 41] **and it is expected that the same would be true of the alakaline earth monochloride ions.**[50] **….**

Barry Sturman's Conclusions

- **The metal monochloride spectra that contribute to the colours of pyrotechnic flames are emitted by neutral metal monochloride molecules, MCl where M is Ba, Ca, Cu or Sr.**
  - **This was clearly stated by Barrow and Caldin[3] as long ago as 1949 and has been confirmed since by Douda,[8–12,39–41] Shimizu,[17–19] and Webster.[21,37,47]**

Barry Sturman's Conclusions

- **The idea that the emitters are singly-charged metal monochloride ions (MCl^+) is erroneous, and can be traced to the 1965 book by Cackett.**[6]
  - **At the time that Cackett wrote his book, no spectra of the monohalide ions of Ba, Ca, or Sr had been reported in the scientific literature,**[41] **none have been reported since**[42] **and there are good reasons for expecting that these ions would not emit visible spectra.**[50] (Continued)

Barry Sturman's Conclusions

- Cackett (Continued)
  - Similarly, there are no reports of spectra of $CuCl^+$;[41,42] the high ionization energy of this ion[51] make it most unlikely that it could exist in a flame in sufficient numbers to contribute in any significant way to the emission of light by the flame.

Metal Monochloride Emitters in Pyrotechnic Flames – IONS or NEUTRALS

THE END

Thank You for Your Attention

If you have questions, Ask Barry:

(bsturman@hyperlink.net.au)

Using Thermodynamic Codes to Simulate Pyrotechnic Reactions

TNO Prins Maurits Laboratory

Contents of Presentation

- Background & problem description
- Aim
- Existing thermodynamic models
- Results
- Discussion
- Conclusions
- Acknowledgements

Background

- From the field of rocket propellants (and explosives) it is well known that thermodynamic models can successfully be used to predict theoretical performance.

- Within the field of pyrotechnics thermodynamic models are used also at times, but in general the reliability of results remains point of discussion.

Problem

- Experimental scientists and engineers may need to explore a certain mixture of ingredients (that is “fixed”), and see what the effects are on the stoichiometry.
- How do we see what the changes are in combustion products and temperature?
- It is a “challenge” to properly describe a pyrotechnic reaction with balanced chemical equations.

Problem example

- If we look for example at the combustion of “Black Powder”. How can we best represent the chemistry of combustion in an equation? Does that allows us to determine what the effect is of molar ratio’s?

Berthelot (1876)

$16\ KNO_3 + 6\ S + 13\ C \rightarrow 5\ K_2SO_4 + 6\ N_2 + K_2S + 11\ CO_2$

Kast (1921)

$74\ KNO_3 + 30\ S + 16\ C_6H_2O$ (charcoal) ? $56\ CO_2 + 14\ CO + 3\ CH_4 + 2\ H_2S + 4\ H_2 + 35\ N_2 + 19\ K_2CO_3 + 7\ K_2SO_4 + 2\ K_2S + 8\ K_2S_2O_3 + 2\ KCNS + (NH_4)_2CO_3 + C + S + 665$ kcal

- Does this work well?
- Are there other or additional ways of doing this?

Aim

- This presentation briefly explores a limited number of pyrotechnic mixtures with different codes. We will be using a limited number of different thermodynamic codes. (ICT Code, Ekvi code, NASA Lewis, PROPEP)

- The first aim of this presentation is to briefly review a number of existing models which can be used in the study of pyrotechnic compositions.

- The second aim of this presentation is to encourage discussion on usefulness and reliability. Where are some of the pitfalls? What model may be more suitable for certain types of pyrotechnic composition than another model?

Thermodynamic models

- **Principle is to find a chemical equilibrium composition from reactants by minimization of free energy (Gibbs energy)**
- **Chemical potential μ**

$$\frac{\partial G}{\partial n_i^\alpha} \equiv \mu_i^\alpha = \mu_i^\alpha(T, P, n_i^\alpha)$$

- **Gibbs-Duhem relation**

$$\sum_{i,\alpha} n_i^\alpha d\mu_i^\alpha = 0$$

  - Refer to
    - Cruise, 1979
    - Gordon, McBride, 1994

Some examples of studies into the use of thermodynamic models for pyro

- Davis, Edward J., “Computer Solution of Pyrotechnic Thermochemistry Problems”, 1st IPS, 1968
- De Yong, L. V., Valenta, F.J.. "Evaluation of Selected Computer Models for Modeling Pyrotechnic and Propellant Devices", NOS-IHTR-1279, ADA213003, September 1989
- de Yong L V and Griffiths T T, "The use of equilibrium and kinetic computer codes to study the combustion of MTV formulations", Proc. 19th IPS Seminar, New Zealand, 1994
- Hahma, A., ‘Theoretical Modelling of Some Pyrotechnic Mixtures’, Int. Symp. On Energetic Material Technology, ADPA Proceeding, 24-27 September 1995
- Farid C. Christo, "Thermochemistry and Kinetics Models for Magnesium/Teflon/Viton Pyrotechnic Compositions", DSTO-TR-0938, December 1999

Which thermodynamic models are there?

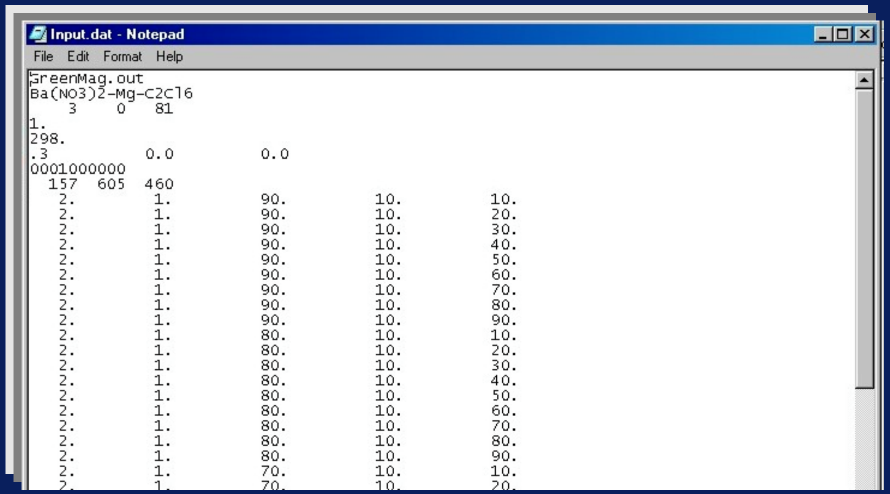
- NASA Lewis (CEA, CET, CEC)
- PROPEP, MICROPEP, GUIPEP
- Ekvi
- ICT Code
- BLAKE
- TIGER
- HSC
- THOR

NASA Lewis Code

- **Early versions (1950 to 1971)**
  - Huff works on methods for computing chemical equilibrium in mid-1940's. See Huff and Calvert (1948) for an example of algebraic reduction method.
  - Huff modifies the Brinkley method, the first formulation in a notation suitable for general problems. Gordon joins in this work (1948). See NACA TN 2113 (1950) and NACA Rep. 1037 (1951) for earliest versions of what eventually became CEC code.
  - Zeleznik joins in this work (1957). See NASA TN D-132 (1959) for first documented code of method described in NACA Rep. 1037, with some improvements, for the IBM 650 data processing system. (according to TN D-132, the first code was created in 1957 and was operational in Jan 1958).
  - See NASA TN D-1454 (1962) and NASA TN D-1737 (1963) for version of the code with applications. Update of the NASA D-132 code for the IBM 704 and 7090. First version to be widely distributed.
  - These 'codes' all used an Equilibrium Constant method (Brinkley-Huff) for deriving the iteration equations for finding chemical equilibrium composition. However, sometime in the 1960's, the switch was made to the minimization of Gibbs function for deriving the chemical equilibrium iteration equations.
- **CEC = Chemical Equilibrium Code (1971 to 1984).**
- **CET = Chemical Equilibrium and Transport Properties (1984 to 1994).**
- **CEA = Chemical Equilibrium and Applications (1994 to present)**

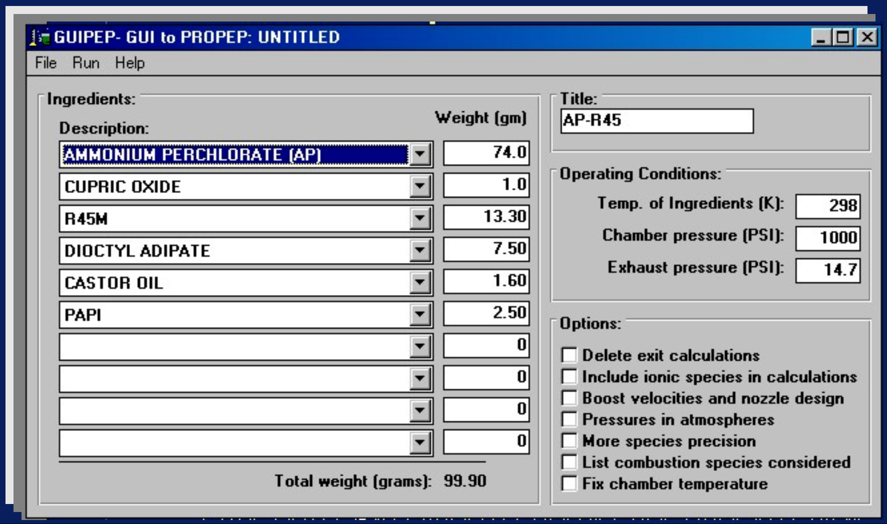
- **http://www.grc.nasa.gov/WWW/CEAWeb/**

PROPEP/MICROPEP & GUIPEP



```
GreenMag.out
Ba(NO3)2-Mg-C2Cl6
    3    0   81
1.
298.
.3          0.0         0.0
0001000000
  157  605  460
   2.         1.         90.         10.         10.
   2.         1.         90.         10.         20.
   2.         1.         90.         10.         30.
   2.         1.         90.         10.         40.
   2.         1.         90.         10.         50.
   2.         1.         90.         10.         60.
   2.         1.         90.         10.         70.
   2.         1.         90.         10.         80.
   2.         1.         90.         10.         90.
   2.         1.         80.         10.         10.
   2.         1.         80.         10.         20.
   2.         1.         80.         10.         30.
   2.         1.         80.         10.         40.
   2.         1.         80.         10.         50.
   2.         1.         80.         10.         60.
   2.         1.         80.         10.         70.
   2.         1.         80.         10.         80.
   2.         1.         80.         10.         90.
   2.         1.         70.         10.         10.
   2.         1.         70.         10.         20.
```

D. R. Cruise, "Theoretical Computations of Equilibrium Compositions, Thermodynamic Properties, and Performance Characteristics of Propellant Systems", NWC-TP-6037, ADA069832, April 1979



Ingredients:

Description:	Weight (gm)
AMMONIUM PERCHLORATE (AP)	74.0
CUPRIC OXIDE	1.0
R45M	13.30
DIOCTYL ADIPATE	7.50
CASTOR OIL	1.60
PAPI	2.50
	0
	0
	0
	0

Total weight (grams): 99.90

Title: AP-R45

Operating Conditions:

Temp. of Ingredients (K): 298

Chamber pressure (PSI): 1000

Exhaust pressure (PSI): 14.7

Options:

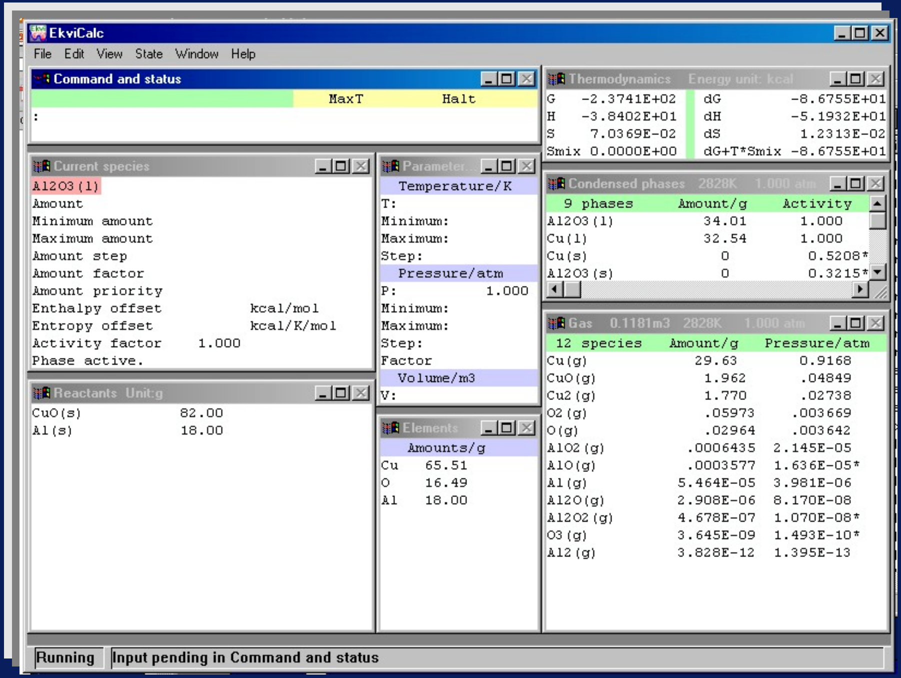
- ☐ Delete exit calculations
- ☐ Include ionic species in calculations
- ☐ Boost velocities and nozzle design
- ☐ Pressures in atmospheres
- ☐ More species precision
- ☐ List combustion species considered
- ☐ Fix chamber temperature

Arthur J. Lekstutis
(c) 1996
Version 0.04 alpha

http://lekstutis.com/Artie/PEP/

Ekvi

- Ekvi can handle systems with up to 15 elements and 500 species (including phases) simultaneously
- Ekvi uses specific commands. Functions partly in Windows



Command and status

```
                              MaxT        Halt
:
```

Current species

```
Al2O3(l)
Amount
Minimum amount
Maximum amount
Amount step
Amount factor
Amount priority
Enthalpy offset            kcal/mol
Entropy offset             kcal/K/mol
Activity factor    1.000
Phase active.
```

Reactants Unit:g

```
CuO(s)              82.00
Al(s)               18.00
```

Parameter...

```
  Temperature/K
T:
Minimum:
Maximum:
Step:
  Pressure/atm
P:             1.000
Minimum:
Maximum:
Step:
Factor
  Volume/m3
V:
```

Elements

```
  Amounts/g
Cu    65.51
O     16.49
Al    18.00
```

Thermodynamics Energy unit: kcal

```
G   -2.3741E+02   dG          -8.6755E+01
H   -3.8402E+01   dH          -5.1932E+01
S    7.0369E-02   dS           1.2313E-02
Smix 0.0000E+00   dG+T*Smix   -8.6755E+01
```

Condensed phases 2828K 1.000 atm

```
  9 phases       Amount/g     Activity
Al2O3(l)            34.01       1.000
Cu(l)               32.54       1.000
Cu(s)                 0         0.5208*
Al2O3(s)              0         0.3215*
```

Gas 0.1181m3 2828K 1.000 atm

```
 12 species     Amount/g    Pressure/atm
Cu(g)             29.63       0.9168
CuO(g)            1.962       .04849
Cu2(g)            1.770       .02738
O2(g)             .05973      .003669
O(g)              .02964      .003642
AlO2(g)         .0006435    2.145E-05
AlO(g)          .0003577    1.636E-05*
Al(g)          5.464E-05    3.981E-06
Al2O(g)        2.908E-06    8.170E-08
Al2O2(g)       4.678E-07    1.070E-08*
O3(g)          3.645E-09    1.493E-10*
Al2(g)         3.828E-12    1.395E-13
```

Running | Input pending in Command and status

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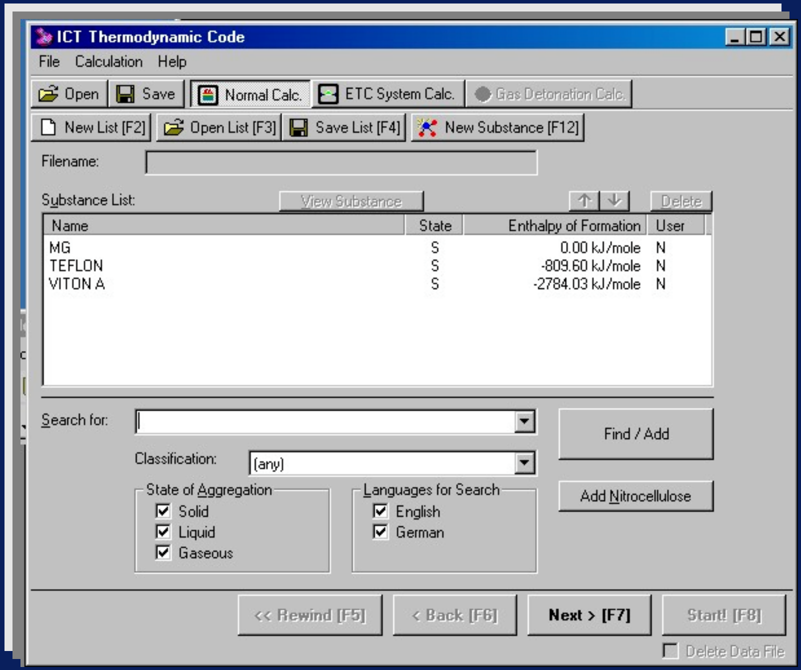
http://www.mkem.uu.se/kurser/MatDes10pK4/

ICT Thermodynamic Code

- Up to 75 reaction products can be present; 40 of these can be in liquid or solid state. Flexible and quick to use in Windows environment. Great ICT Database to work with (separate)



Filename:

Substance List:

Name	State	Enthalpy of Formation	User
MG	S	0.00 kJ/mole	N
TEFLON	S	-809.60 kJ/mole	N
VITON A	S	-2784.03 kJ/mole	N

Search for:

Classification: (any)

State of Aggregation
☑ Solid
☑ Liquid
☑ Gaseous

Languages for Search
☑ English
☑ German

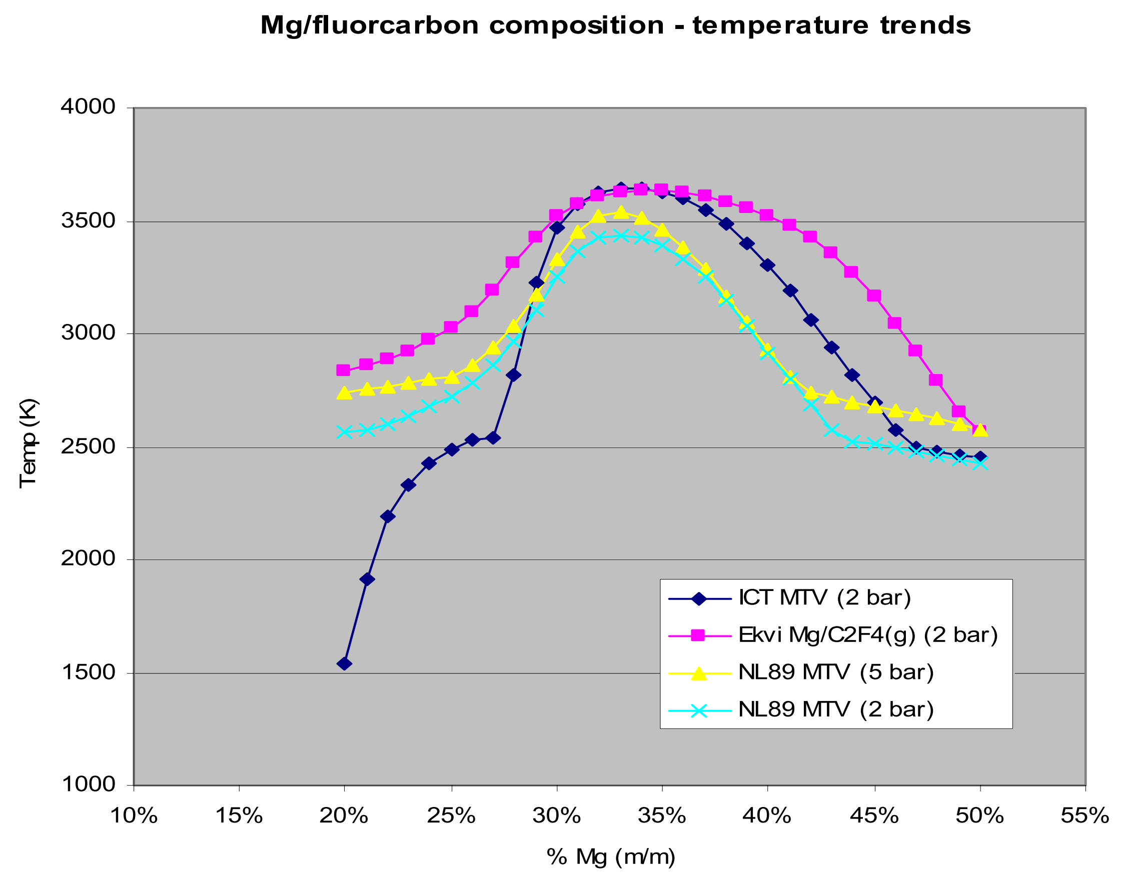
☐ Delete Data File

http://www.ict.fhg.de/english/scope/em/ecode.html

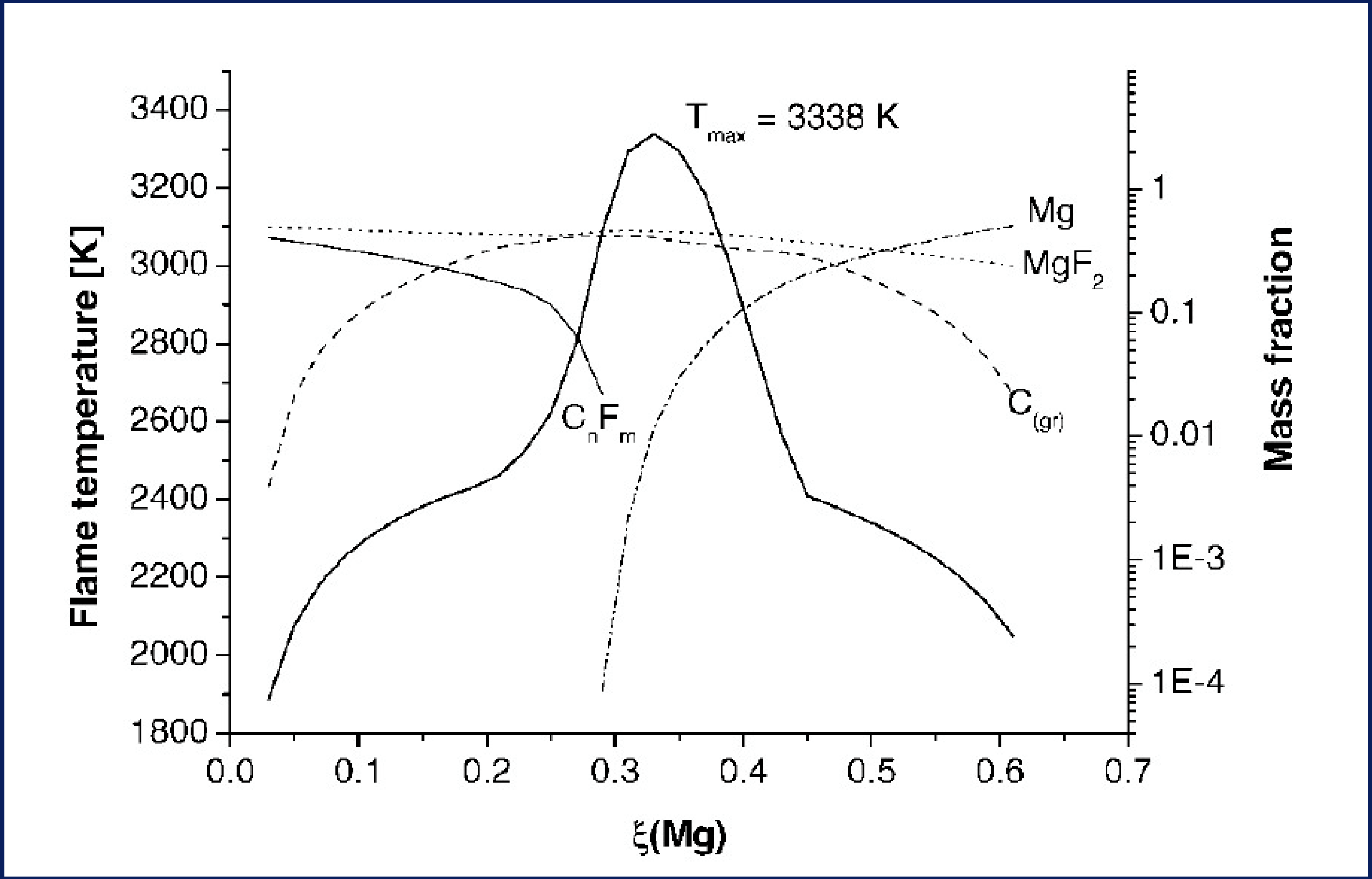
Examples

- Mg/Teflon/Viton
- AP/NC/$CaCO_3$
- Black Powder
- Al2O3/Al
- CuO/Al
- B/KNO3

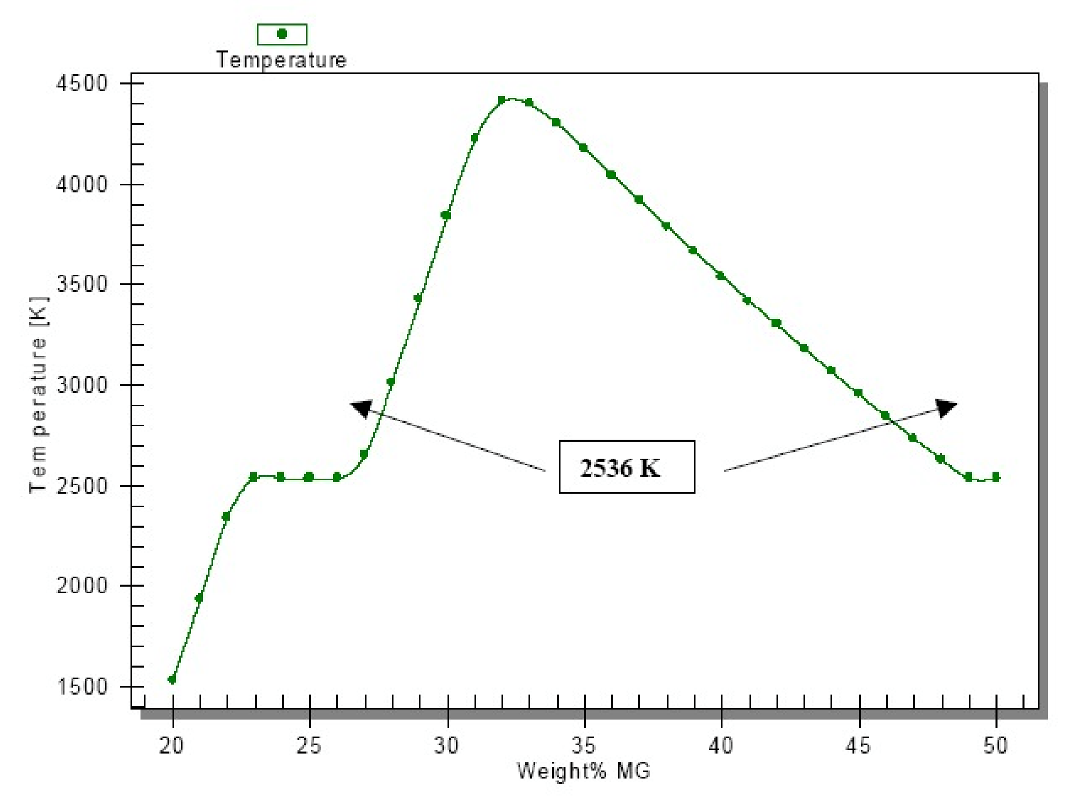
MTV Results (ICT Code, Ekvi, NASA-Lewis)



MTV Simulations by Koch, *PEP 27*, 2002



MTV Simulations in ICT Code Manual



2536 K is boiling temperature of MgF2 (l)

Figure taken from Manual ICT Code

AP/NC/CaCO$_3$ (Presented IPS2002)

- **Calcium based orange/red color composition**
  - Composition chosen because of low number of ingredients and ease to process in small quantities, low toxicity and low cost.

	Weight %
Ammonium perchlorate NH_4ClO_4	**76**
Cellulose $C_6H_{10}O_5$	**22**
Cellulose nitrate $C_6H_{7.41}N_{2.58}O_{10.17}$	**2**
Calcium carbonate $CaCO_3$	**+ 1 - 20**

Base composition

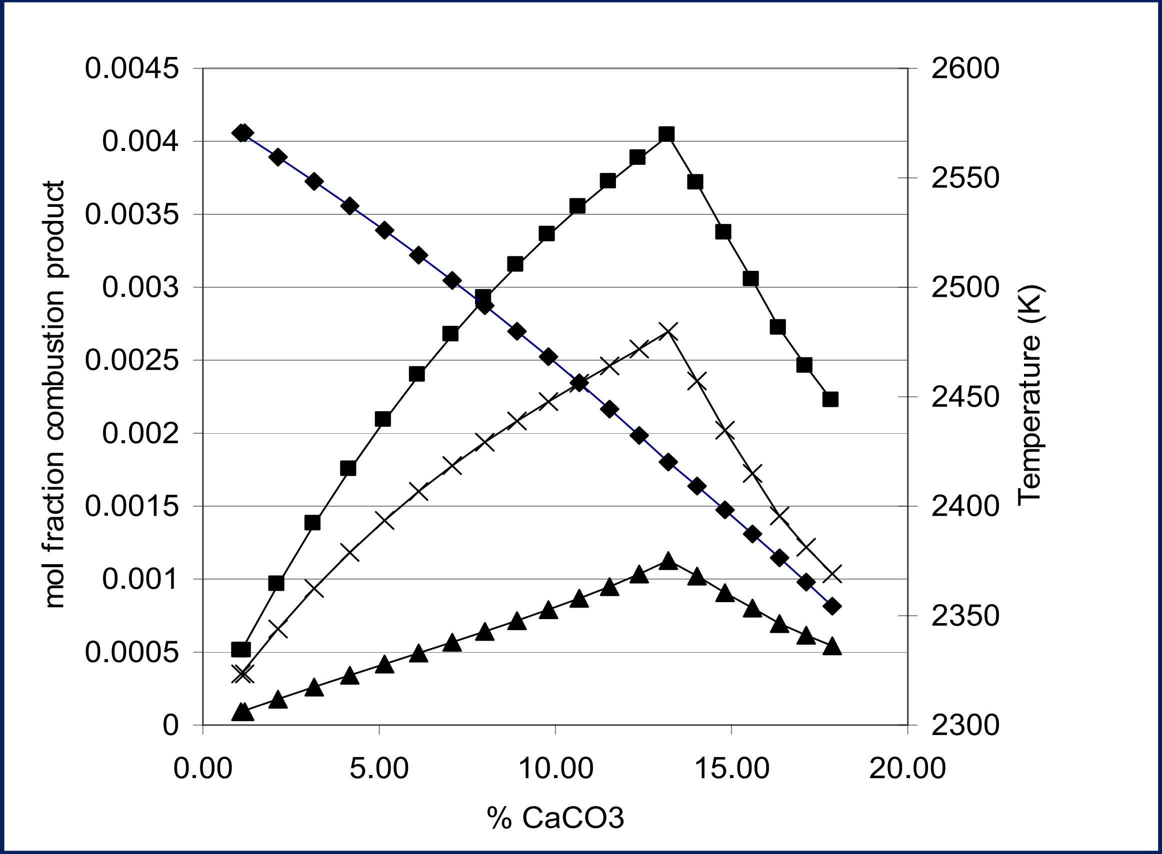
AP/NC/$CaCO_3$ specific interest

- **Thermodynamic calculations with ICT-Thermodynamic code**
  - Relevant reaction products considered in simulations:
    - CaO, CaOH, CaCl
  - CaCl emits between 605 and 635 nm
  - CaO emits broad bands between 598 and 636 nm
  - CaOH very diffuse with a maximum at 623 nm, and weaker diffuse bands at 603 and 641nm and a band near 555 nm

  - Thermodynamic calculations performed on ‘base composition’ (NH_4ClO_4/cellulose/cellulose nitrate) with varying weight % $CaCO_3$ (0-20).

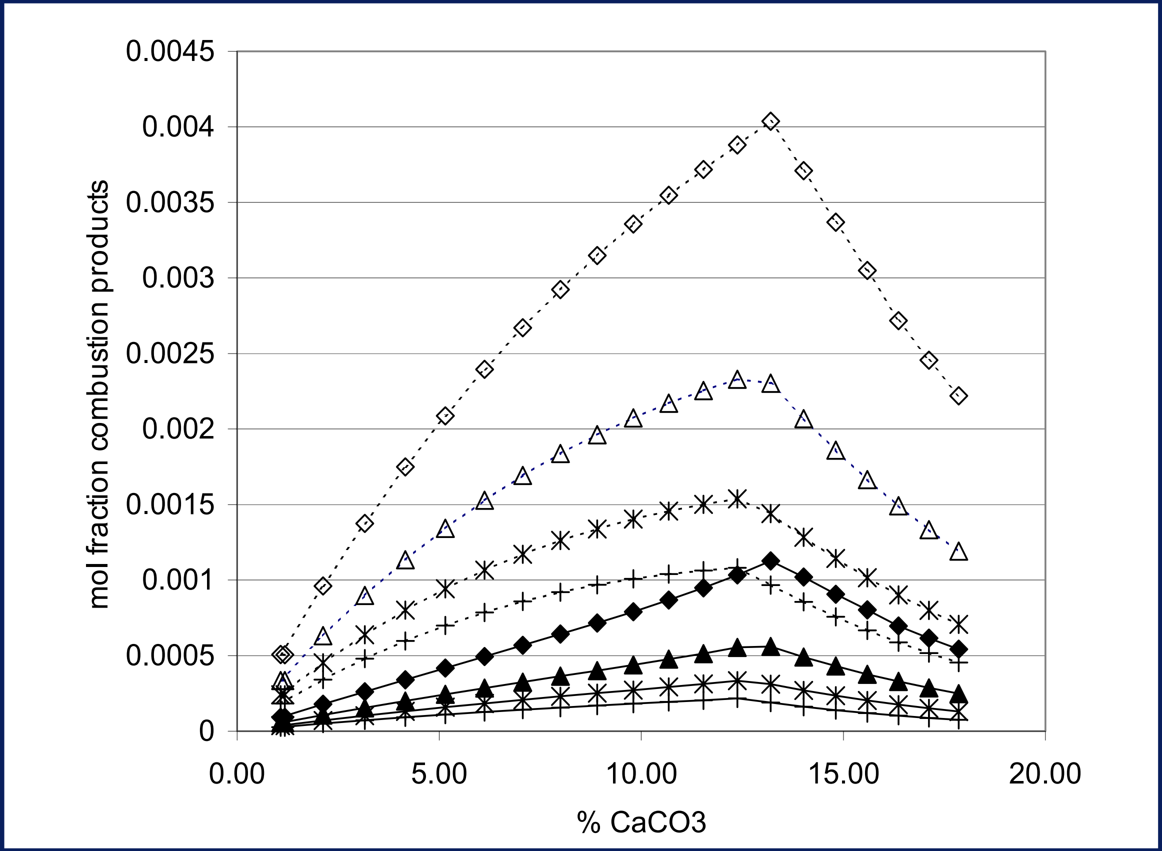
AP/NC/CaCO$_3$ Results

- **Reaction products and temperature at 1.0 bar**
  - □CaCl; □ CaOH; and X CaO(g) (x 100); ♦temperature



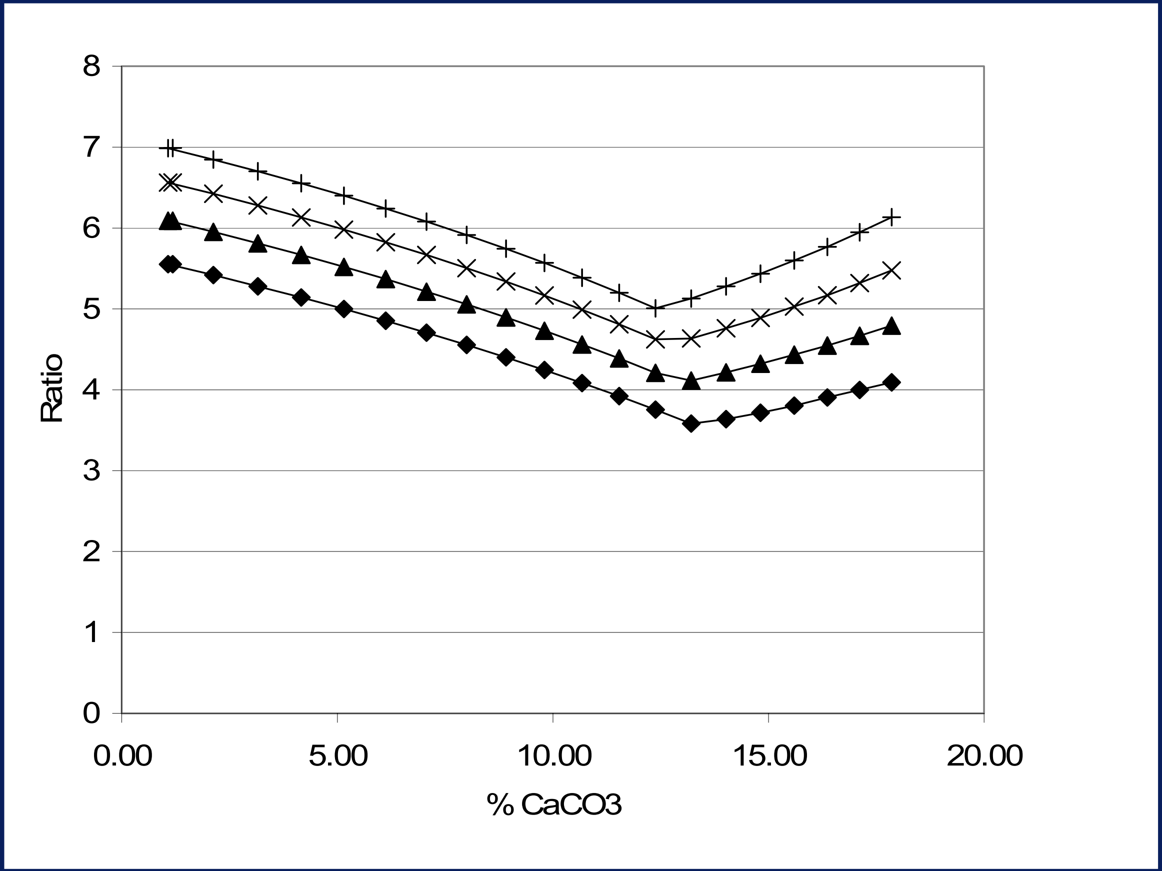
AP/NC/$CaCO_3$ Results

- **Mole fractions of combustion products at different pressures**
  - dashed line CaCl, normal line CaOH; ♦ 1.0 bar; □ 1.5 bar; **X** 2.0 bar; + 2.5 bar



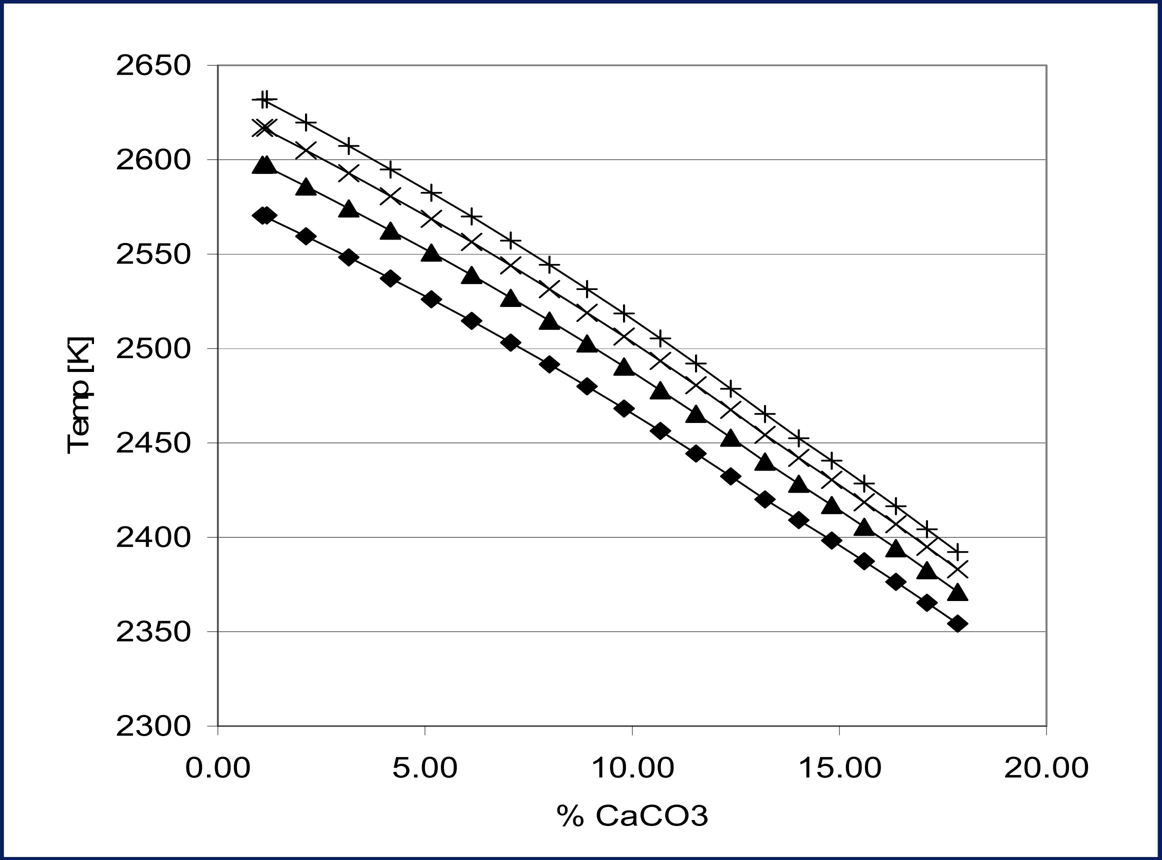
AP/NC/CaCO$_3$ Results

- **Pressure dependency of ratio CaCl / CaOH**
  - dashed line CaCl, normal line CaOH; ♦ 1.0 bar; □ 1.5 bar; **X** 2.0 bar; + 2.5 bar



AP/NC/CaCO$_3$ Results

- **Pressure dependency of reaction temperature**
  - ♦ 1.0 bar; □ 1.5 bar; **X** 2.0 bar; + 2.5 bar

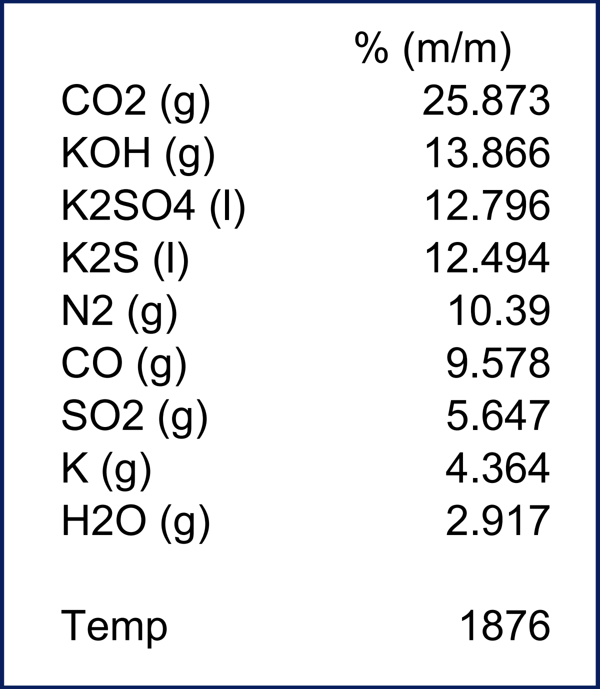


AP/NC/$CaCO_3$ Conclusions

- **Results of simulation show that**
  - The mole fractions of CaCl and CaOH are approximately similar
  - The mole fraction of CaO (g) was about 1% of CaCl and CaOH
  - The mole fractions of CaCl, CaOH and CaO decrease with increasing pressure
  - The effect of additional percentages $CaCO_3$ (between 1 and 20) on temperature is stronger than the effect of pressure (between 1 and 2.5 bars)
  - There was a limited influence of the pressure on the ratio between CaCl/CaOH

Black Powder

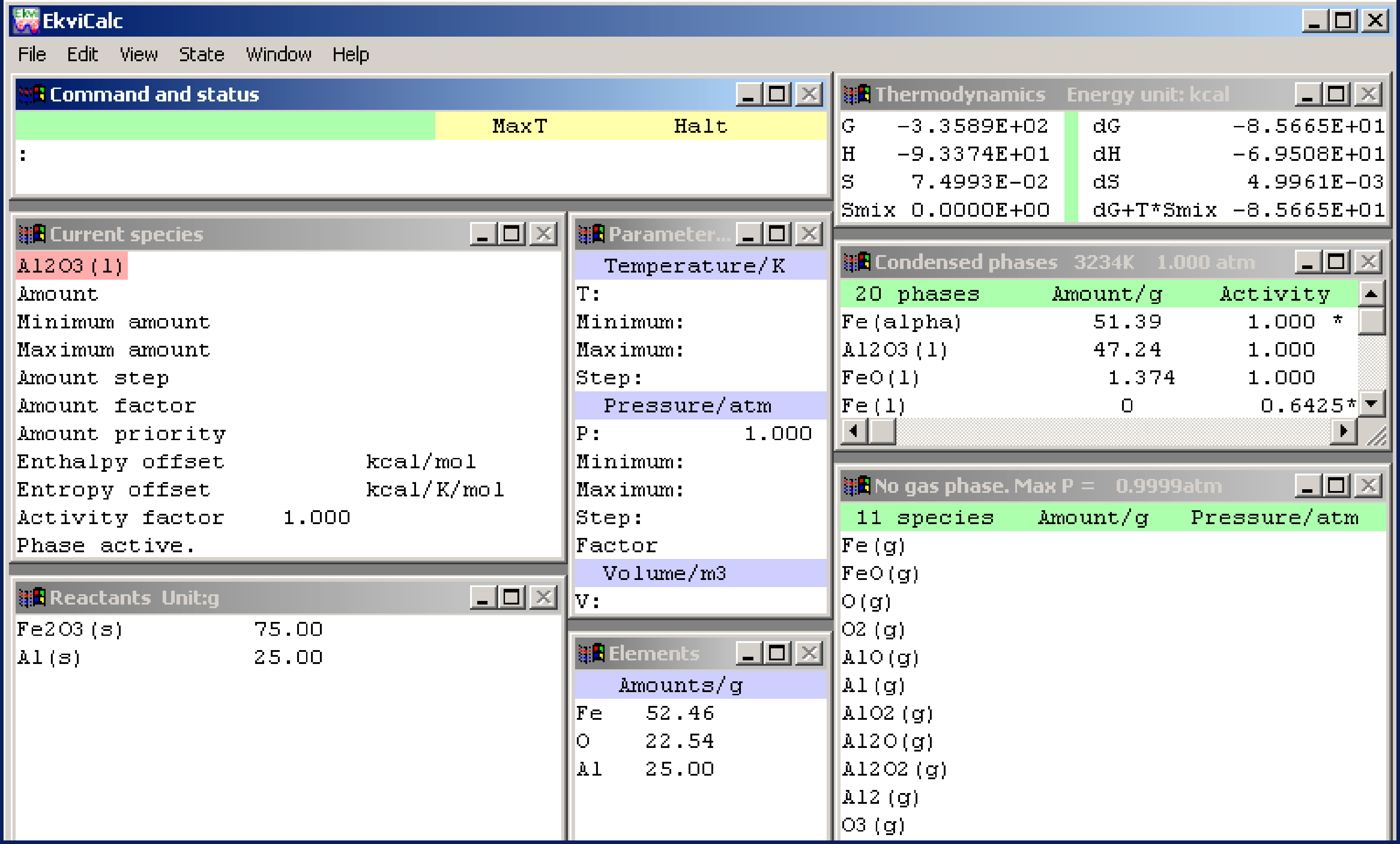
- ICT Code
- Pressure 3 bar



	% (m/m)
CO2 (g)	25.873
KOH (g)	13.866
K2SO4 (l)	12.796
K2S (l)	12.494
N2 (g)	10.39
CO (g)	9.578
SO2 (g)	5.647
K (g)	4.364
H2O (g)	2.917
Temp	1876

- Ekvi gives an example of BP combustion but assumes charcoal ~ C. The example given uses wrong %S, but both in example with correct formulation, it predicts no KOH(g)

Fe2O3/Al thermite



Thermodynamics Energy unit: kcal

```
G    -3.3589E+02   dG          -8.5665E+01
H    -9.3374E+01   dH          -6.9508E+01
S     7.4993E-02   dS           4.9961E-03
Smix  0.0000E+00   dG+T*Smix   -8.5665E+01
```

Current species

```
Al2O3(l)
Amount
Minimum amount
Maximum amount
Amount step
Amount factor
Amount priority
Enthalpy offset                 kcal/mol
Entropy offset                  kcal/K/mol
Activity factor       1.000
Phase active.
```

Parameters

```
 Temperature/K
T:
Minimum:
Maximum:
Step:
 Pressure/atm
P:              1.000
Minimum:
Maximum:
Step:
Factor
 Volume/m3
V:
```

Condensed phases 3234K 1.000 atm

```
 20 phases       Amount/g     Activity
Fe(alpha)          51.39       1.000 *
Al2O3(l)           47.24       1.000
FeO(l)              1.374      1.000
Fe(l)              0           0.6425*
```

No gas phase. Max P = 0.9999atm

```
 11 species     Amount/g     Pressure/atm
Fe(g)
FeO(g)
O(g)
O2(g)
AlO(g)
Al(g)
AlO2(g)
Al2O(g)
Al2O2(g)
Al2(g)
O3(g)
```

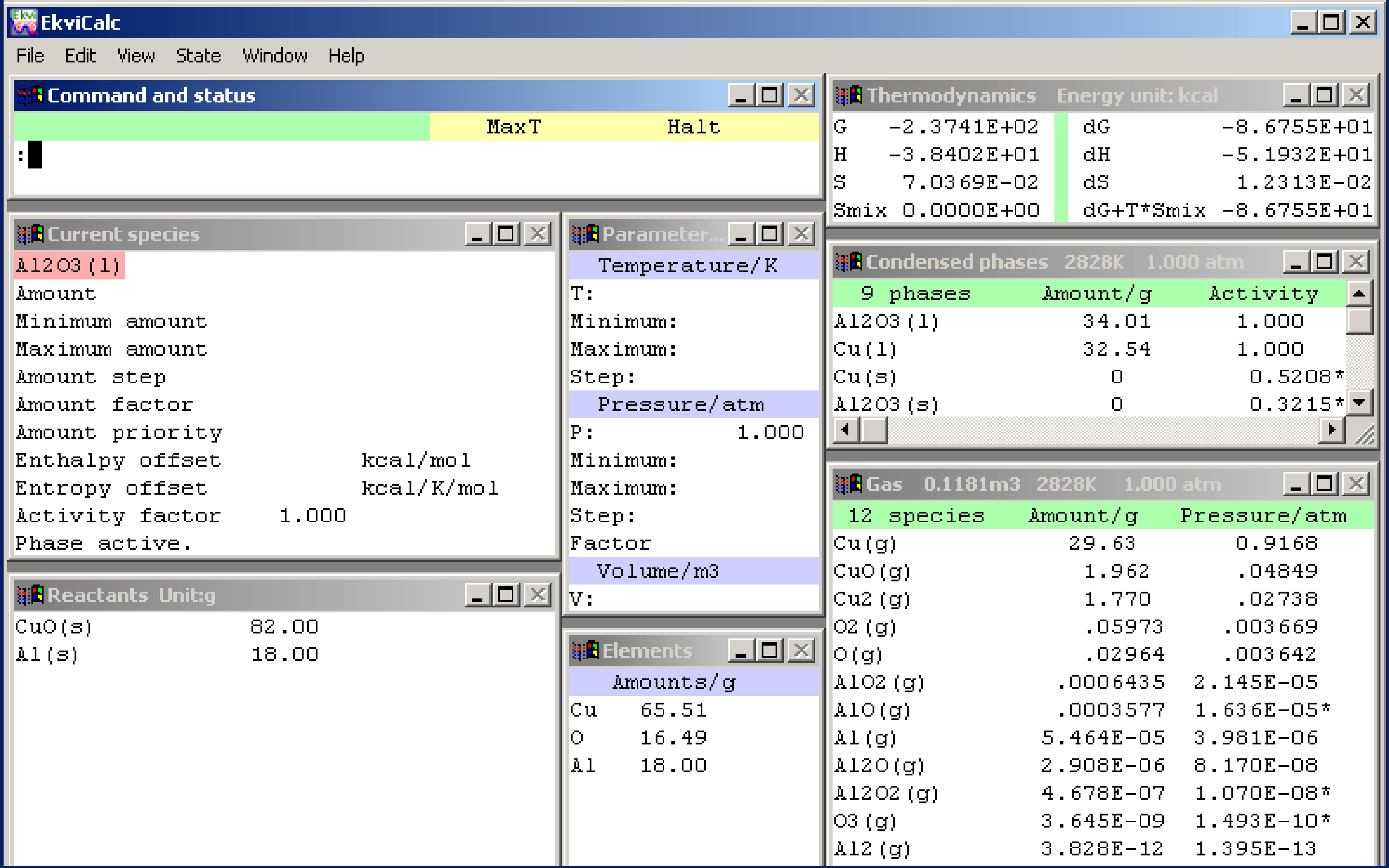
Reactants Unit:g

```
Fe2O3(s)       75.00
Al(s)          25.00
```

Elements

```
  Amounts/g
Fe    52.46
O     22.54
Al    25.00
```

CuO/Al



Command and status

MaxT Halt

:

Thermodynamics Energy unit: kcal

G	-2.3741E+02	dG	-8.6755E+01
H	-3.8402E+01	dH	-5.1932E+01
S	7.0369E-02	dS	1.2313E-02
Smix	0.0000E+00	dG+T*Smix	-8.6755E+01

Current species

Al2O3(l)
Amount
Minimum amount
Maximum amount
Amount step
Amount factor
Amount priority
Enthalpy offset kcal/mol
Entropy offset kcal/K/mol
Activity factor 1.000
Phase active.

Parameter...

Temperature/K
T:
Minimum:
Maximum:
Step:
Pressure/atm
P: 1.000
Minimum:
Maximum:
Step:
Factor
Volume/m3
V:

Condensed phases 2828K 1.000 atm

9 phases	Amount/g	Activity
Al2O3(l)	34.01	1.000
Cu(l)	32.54	1.000
Cu(s)	0	0.5208*
Al2O3(s)	0	0.3215*

Reactants Unit:g

CuO(s)	82.00
Al(s)	18.00

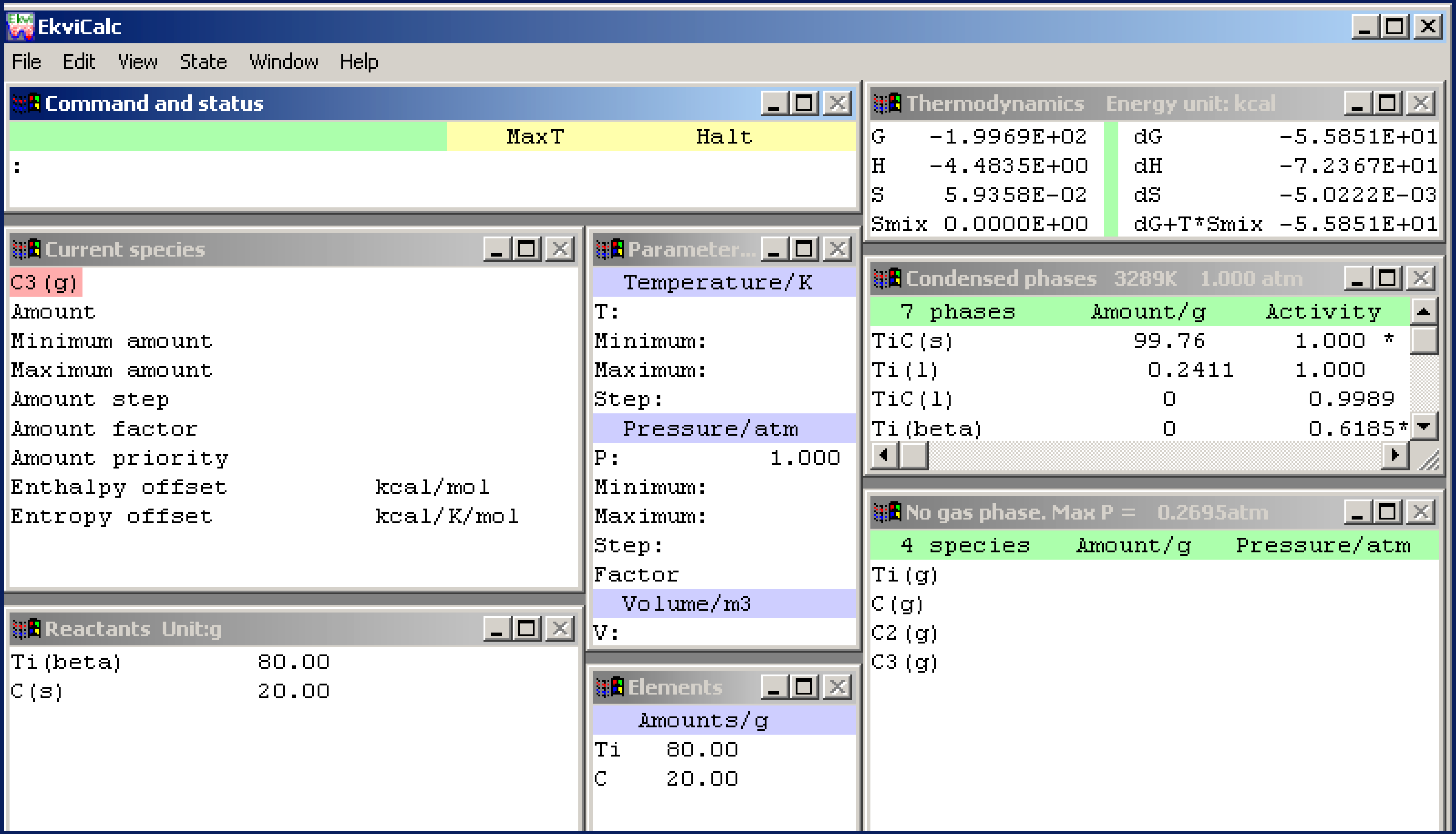
Elements

	Amounts/g
Cu	65.51
O	16.49
Al	18.00

Gas 0.1181m3 2828K 1.000 atm

12 species	Amount/g	Pressure/atm
Cu(g)	29.63	0.9168
CuO(g)	1.962	.04849
Cu2(g)	1.770	.02738
O2(g)	.05973	.003669
O(g)	.02964	.003642
AlO2(g)	.0006435	2.145E-05
AlO(g)	.0003577	1.636E-05*
Al(g)	5.464E-05	3.981E-06
Al2O(g)	2.908E-06	8.170E-08
Al2O2(g)	4.678E-07	1.070E-08*
O3(g)	3.645E-09	1.493E-10*
Al2(g)	3.828E-12	1.395E-13

Ti/C intermetallic



Command and status

```
                              MaxT        Halt
:
```

Thermodynamics   Energy unit: kcal

```
G    -1.9969E+02    dG          -5.5851E+01
H    -4.4835E+00    dH          -7.2367E+01
S     5.9358E-02    dS          -5.0222E-03
Smix  0.0000E+00    dG+T*Smix   -5.5851E+01
```

Current species

```
C3(g)
Amount
Minimum amount
Maximum amount
Amount step
Amount factor
Amount priority
Enthalpy offset          kcal/mol
Entropy offset           kcal/K/mol
```

Parameter...

```
 Temperature/K
T:
Minimum:
Maximum:
Step:
 Pressure/atm
P:           1.000
Minimum:
Maximum:
Step:
Factor
 Volume/m3
V:
```

Condensed phases 3289K   1.000 atm

```
 7 phases      Amount/g     Activity
TiC(s)           99.76       1.000 *
Ti(l)             0.2411     1.000
TiC(l)            0          0.9989
Ti(beta)          0          0.6185*
```

No gas phase. Max P = 0.2695atm

```
 4 species    Amount/g    Pressure/atm
Ti(g)
C(g)
C2(g)
C3(g)
```

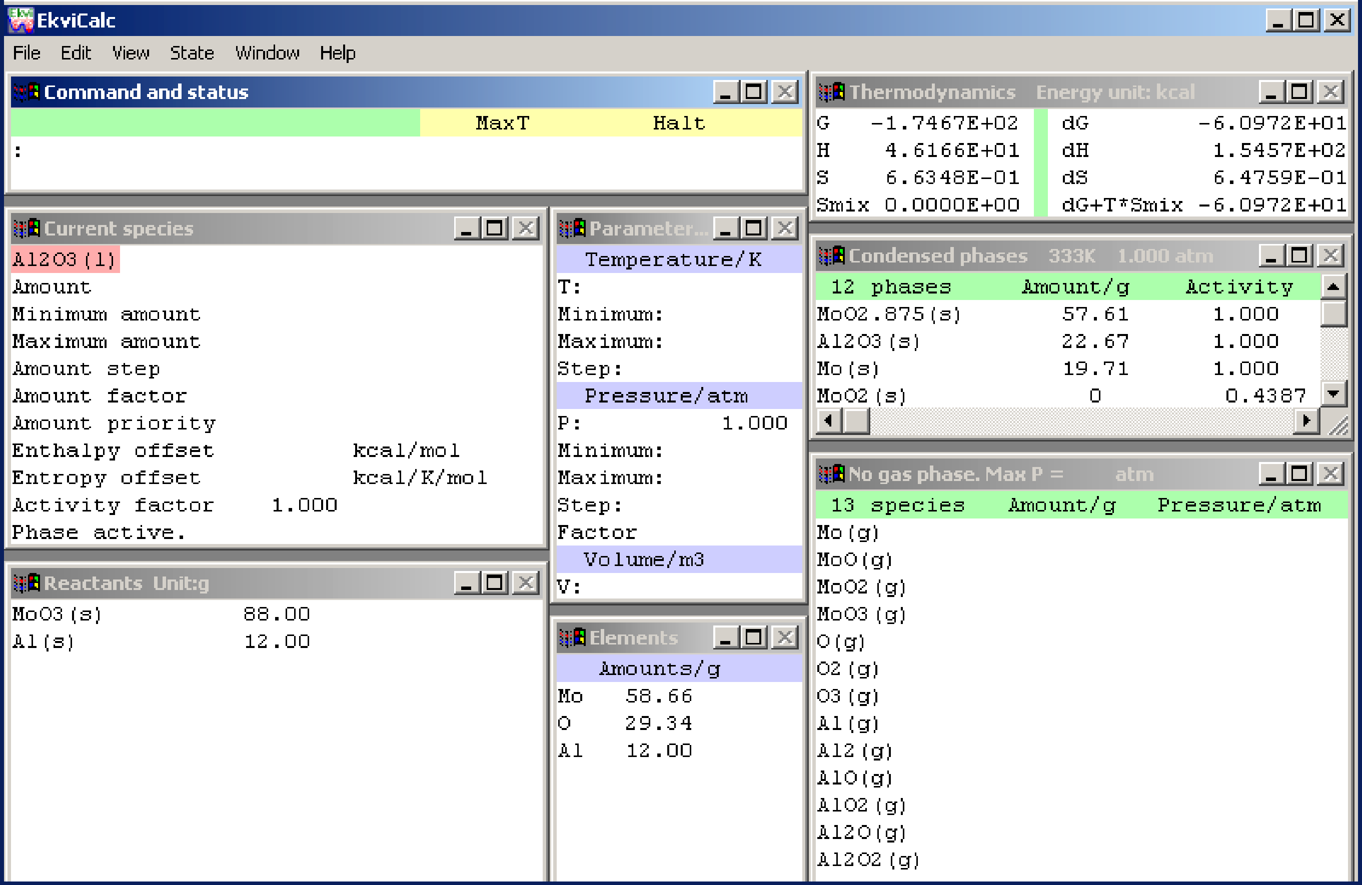
Reactants Unit:g

```
Ti(beta)        80.00
C(s)            20.00
```

Elements

```
  Amounts/g
Ti    80.00
C     20.00
```

MoO3/Al thermite



```
Command and status
MaxT          Halt
:
```

```
Thermodynamics   Energy unit: kcal
G    -1.7467E+02   dG          -6.0972E+01
H     4.6166E+01   dH           1.5457E+02
S     6.6348E-01   dS           6.4759E-01
Smix  0.0000E+00   dG+T*Smix   -6.0972E+01
```

```
Current species
Al2O3(l)
Amount
Minimum amount
Maximum amount
Amount step
Amount factor
Amount priority
Enthalpy offset               kcal/mol
Entropy offset                kcal/K/mol
Activity factor      1.000
Phase active.
```

```
Parameter...
  Temperature/K
T:
Minimum:
Maximum:
Step:
  Pressure/atm
P:              1.000
Minimum:
Maximum:
Step:
Factor
  Volume/m3
V:
```

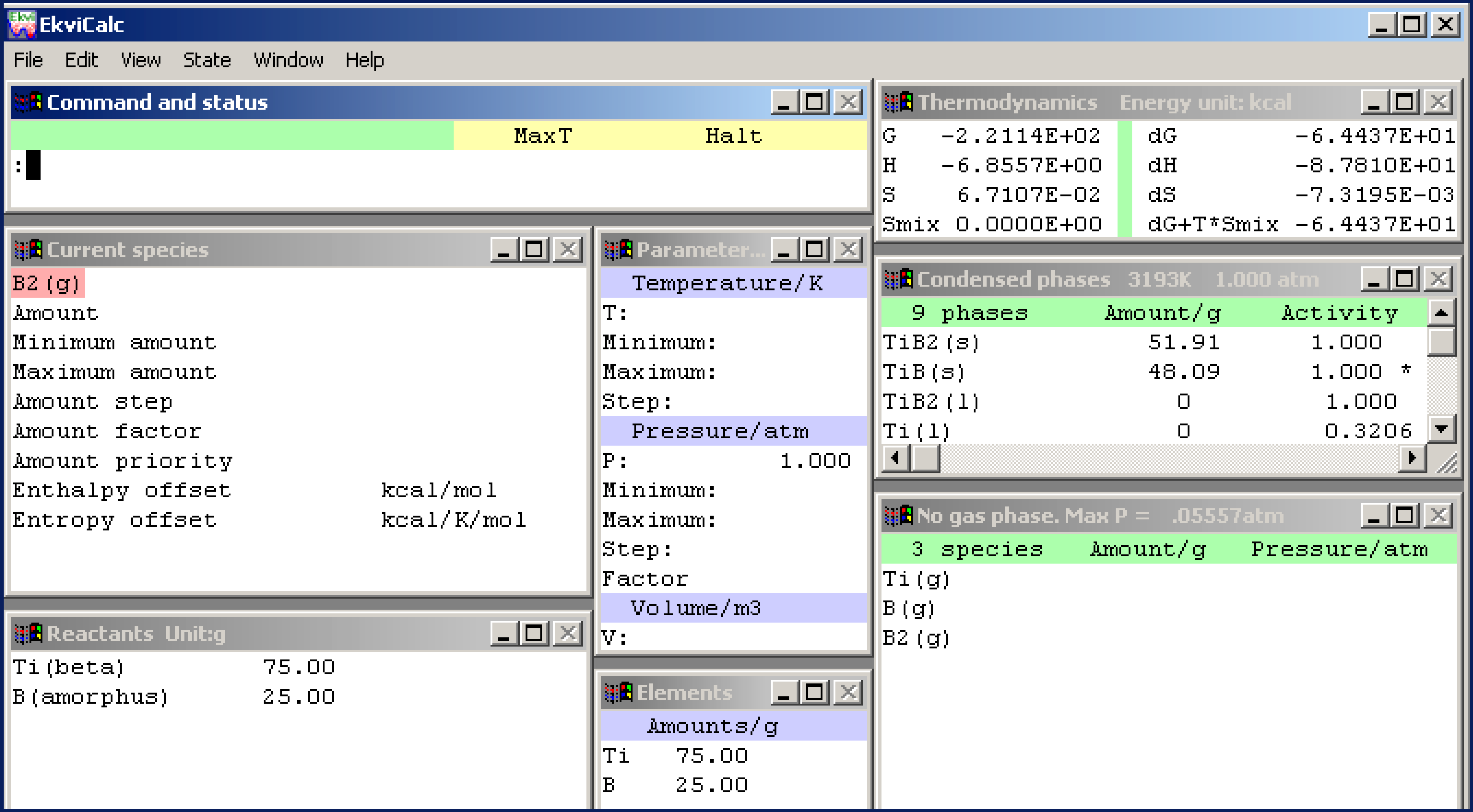
```
Condensed phases   333K   1.000 atm
 12 phases      Amount/g    Activity
MoO2.875(s)      57.61       1.000
Al2O3(s)         22.67       1.000
Mo(s)            19.71       1.000
MoO2(s)              0       0.4387
```

```
No gas phase. Max P =       atm
 13 species     Amount/g    Pressure/atm
Mo(g)
MoO(g)
MoO2(g)
MoO3(g)
O(g)
O2(g)
O3(g)
Al(g)
Al2(g)
AlO(g)
AlO2(g)
Al2O(g)
Al2O2(g)
```

```
Reactants  Unit:g
MoO3(s)          88.00
Al(s)            12.00
```

```
Elements
   Amounts/g
Mo    58.66
O     29.34
Al    12.00
```

Ti/B intermetallic



Command and status

```
                          MaxT        Halt
:
```

Thermodynamics   Energy unit: kcal

```
G     -2.2114E+02   dG           -6.4437E+01
H     -6.8557E+00   dH           -8.7810E+01
S      6.7107E-02   dS           -7.3195E-03
Smix  0.0000E+00    dG+T*Smix    -6.4437E+01
```

Current species

```
B2(g)
Amount
Minimum amount
Maximum amount
Amount step
Amount factor
Amount priority
Enthalpy offset             kcal/mol
Entropy offset              kcal/K/mol
```

Parameter...

```
 Temperature/K
T:
Minimum:
Maximum:
Step:
 Pressure/atm
P:           1.000
Minimum:
Maximum:
Step:
Factor
 Volume/m3
V:
```

Condensed phases   3193K   1.000 atm

```
 9 phases        Amount/g     Activity
TiB2(s)             51.91        1.000
TiB(s)              48.09        1.000 *
TiB2(l)                0         1.000
Ti(l)                  0         0.3206
```

No gas phase. Max P = .05557atm

```
 3 species     Amount/g     Pressure/atm
Ti(g)
B(g)
B2(g)
```

Reactants Unit:g

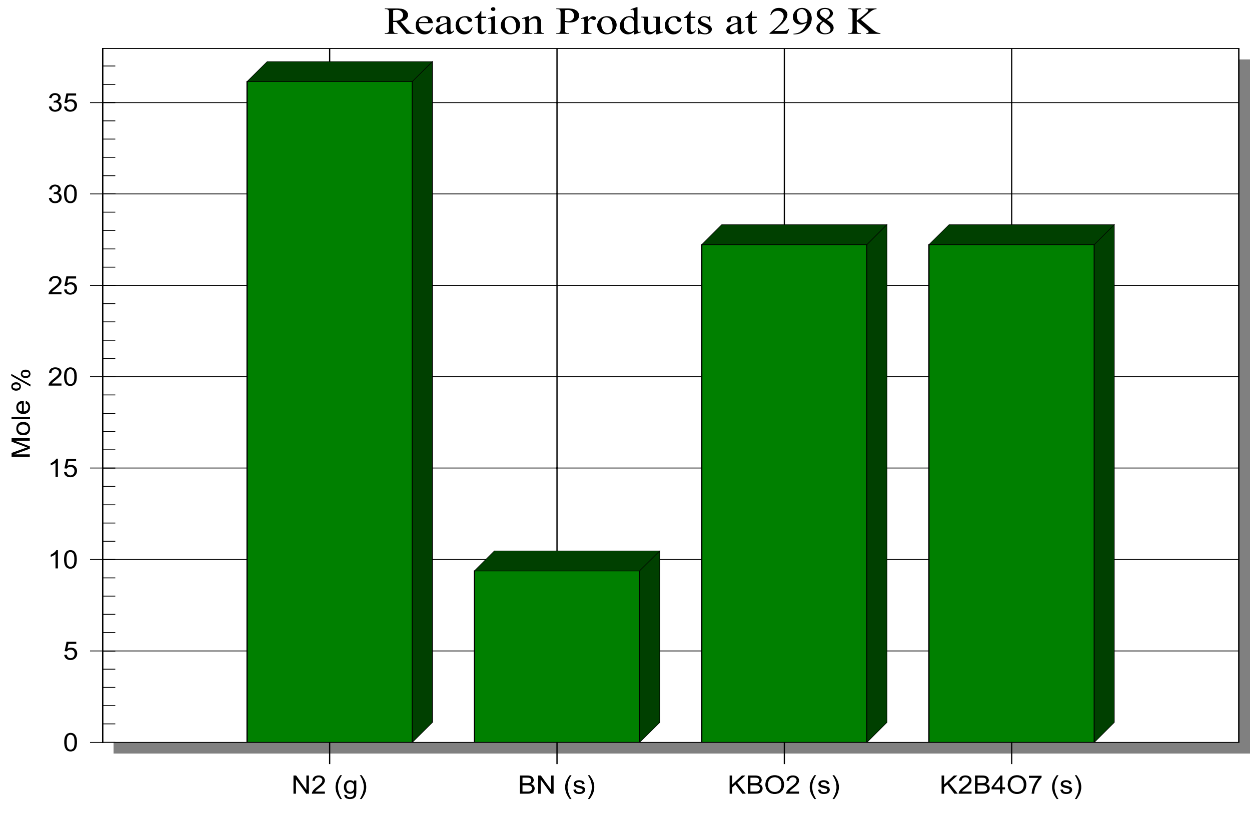
```
Ti(beta)           75.00
B(amorphus)        25.00
```

Elements

```
   Amounts/g
Ti     75.00
B      25.00
```

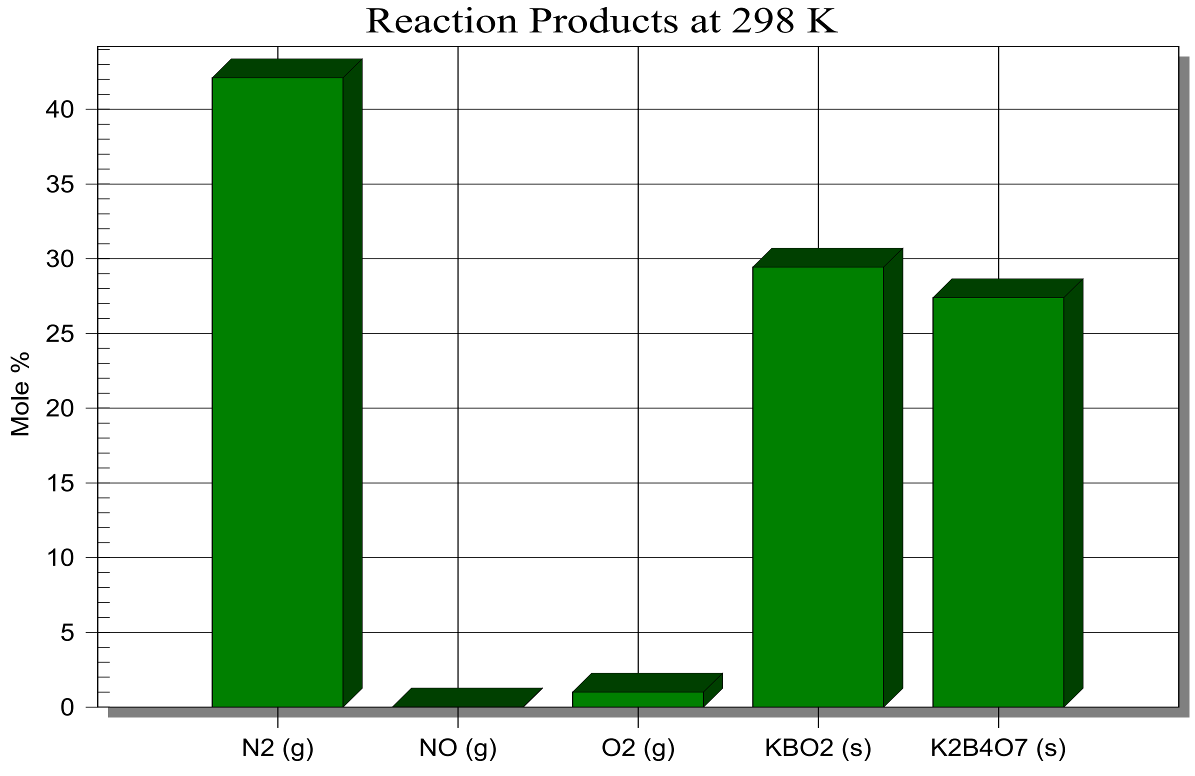
B/KNO3 (ICT Code)

- **16/84 B/KNO3**



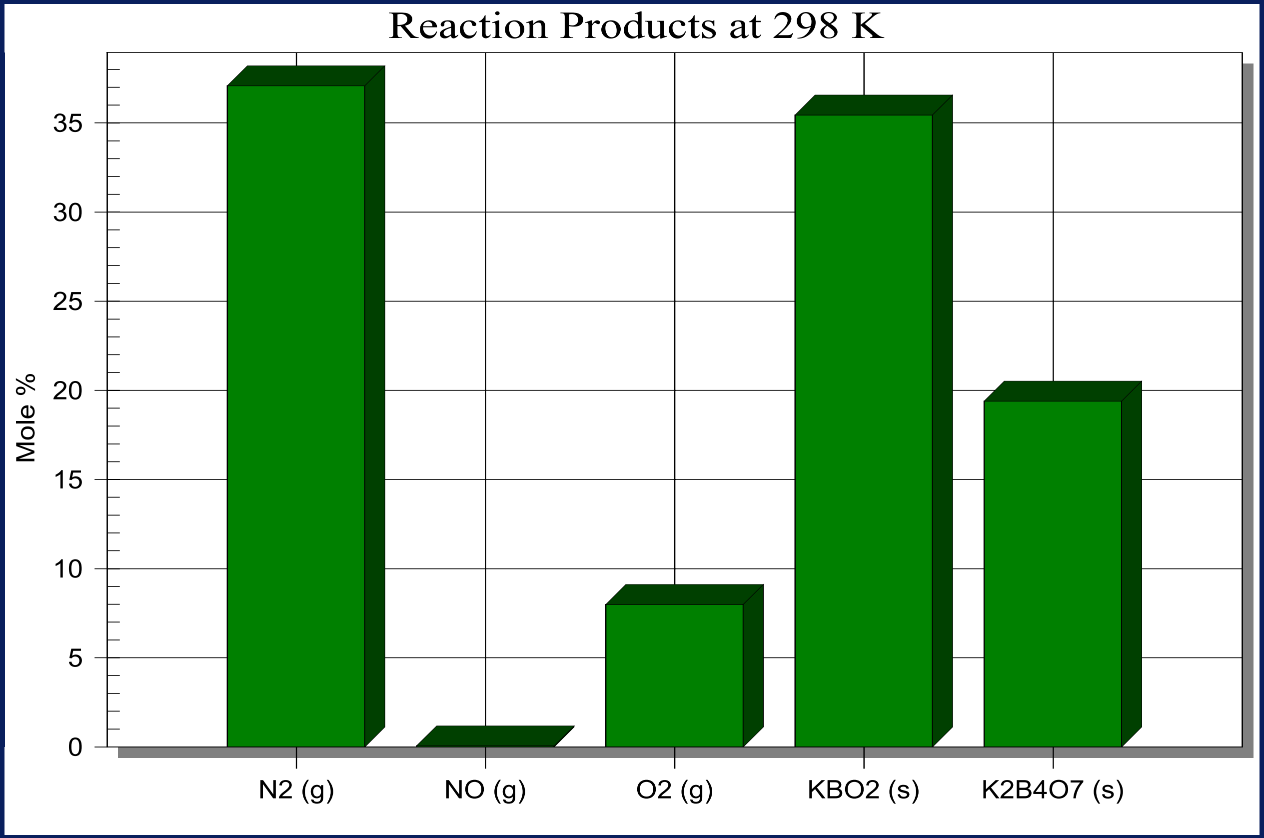
B/KNO3 (ICT Code)

- **15/85 B/KNO3**



B/KNO3 (ICT Code)

- **14/86 B/KNO3**



Conclusion in General

- **Thermodynamic models are not suited for pyrotechnic compositions which**
  - produce relatively high percentages of solid species upon combustion. Programs in general tend to "hang" i.e. not being able to converge to a solution for the equilibrium. The exception to the rule seems to be the Ekvi code. Ekvi generally has less problems to converge, but it has a limited standard database.
  - contain not well defined (chemically and ΔH_f) ingredients such as "Red Gum". It results in unreliable results.

- **Thermodynamic models are suited for pyrotechnic compositions**
  - Especially for compositions that are well understood, or closely related to compositions that have already been studied

Discussion

- Thermodynamic modeling in itself does not yield any information about the kinetics of the system. This is a limitation.

- TNO's interest in thermodynamic modeling of pyrotechnics is linked to the topic of being able to predict IR emission from pyrotechnic compositions.
- Results of thermodynamic modeling are used as input in IR emission models (see Thursday 15th July 11:40)

- **More studies are needed to determine which models are most suitable for given types of pyrotechnic compositions**

References and Further Reading

- Koch, E.-C., “Metal-Fluorocarbon-Pyrolants IV: Thermochemical and Combustion Behaviour of Magnesium/Teflon/Viton (MTV)”, *Propellants, Explosives, Pyrotechnics 27*, 340 - 351 (2002)
- Bathelt, H., Volk, V., Weindel, M., "The ICT-Thermodynamic-Code (ICT Code), User's Manual", Windows v.1, 2000
- Dolata, D.P., “Prediction of Flame Temperatures, Part 1: Low Temperature Reactions”, J. Pyrotechnics 1, 1995
- F. Rigas, N. Pitsinis, e.a., “The Gibbs Energy Minimization Approach in the Estimation of Detonation, Explosion and Work Production Parameters of Confined Charges”, *Propellants, Explosives, Pyrotechnics 19,* 76-81 (1994)
- S. Gordon and B. J. McBride, “Computer Program for Calculating of Complex Chemical Equilibrium Compositions and Applications. I. Analysis”, NASA Reference Publication 1311, October 1994
- E.D. Brown, “An Introduction to PROPEP, a propellant evaluation program for personal computers”, Journal of Pyrotechnics 1, 1995

The End

Fast emission spectroscopy for a better understanding of pyrotechnic combustion behaviors

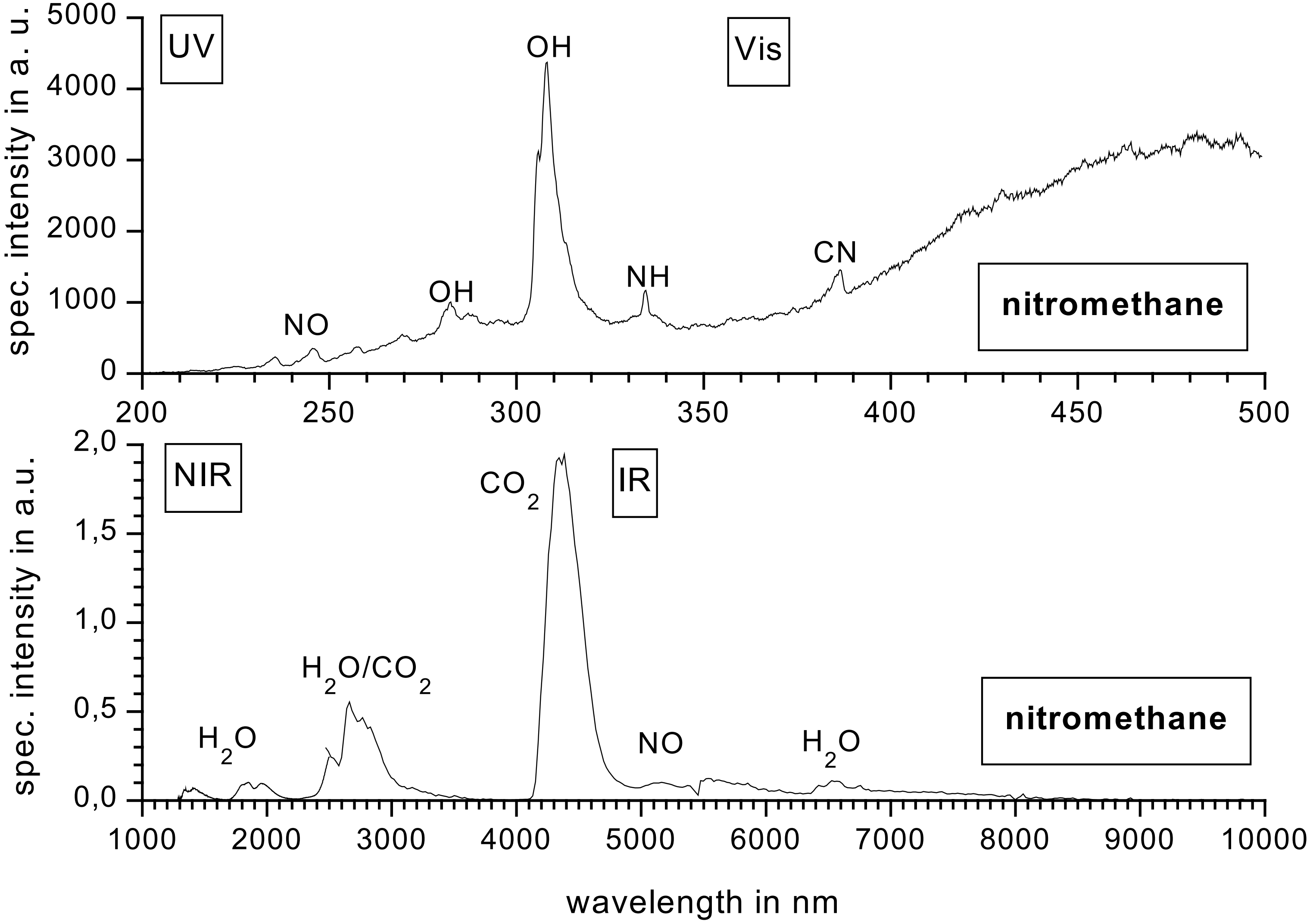
Volker Weiser

Contributors
Norbert Eisenreich, Willi Eckl, Stefan Kelzenberg, Martin Weindel, Evelin Roth, Andrea Baier, Yvonne Plitzko

Index

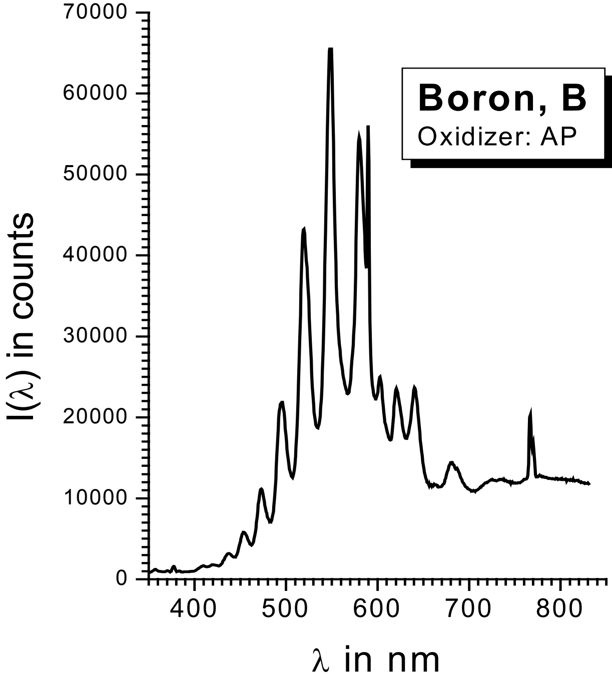
- Scope
- Pyrometers and Spectrographs
- Spectra modelling and data analysis
- Further Examples

Spectra in UV, Vis and (N)IR of nitromethane

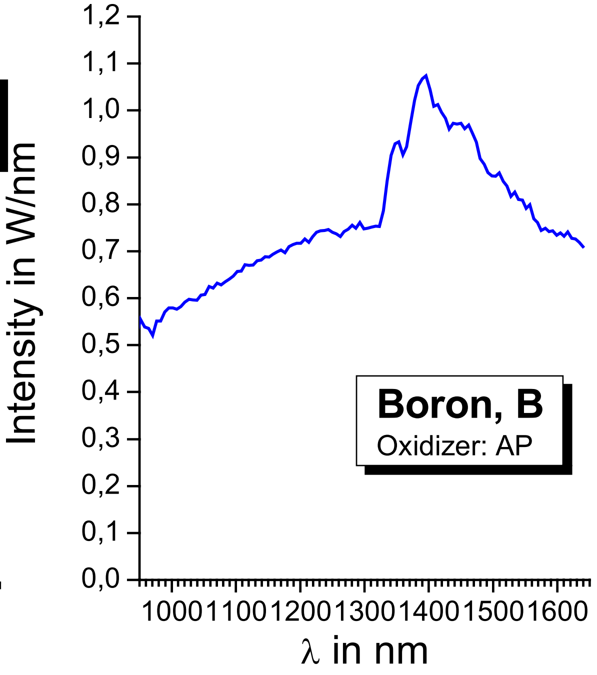


Spectra of Boron-combustion (Oxidisor: AP)

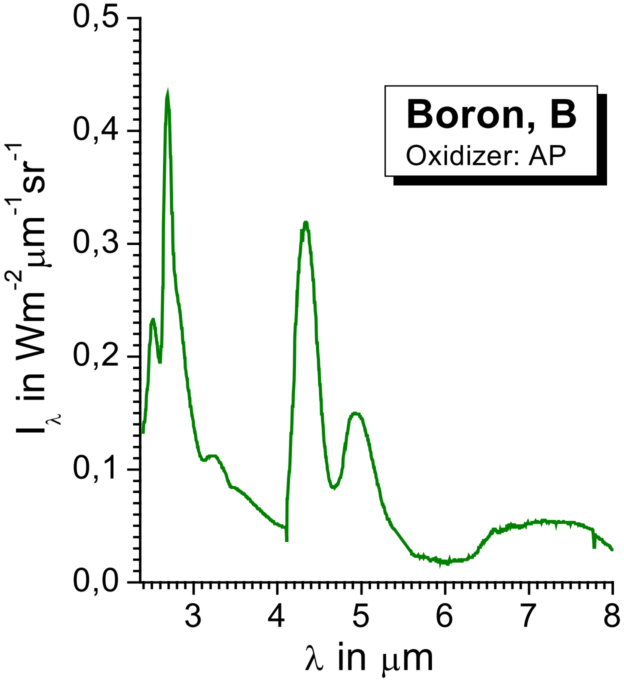
visible



NIR



IR



Emission spectroscopy: Motivation

Aimed properties

•emitting species
•spectral radiation
•temperature
•concentrations

Advantages

+high time resolution
+local distribution
+non-intrusive
+low experimental expense
+robust nature

Disadvantages

-overlapping of bands
-poor spatial resolution
-E/A-behaviour of emitting gases
-self absorption

Pyrometers and Spectrographs

High Speed 2 Colour Pyrometer

ICT-development

Non-intrusive emission- and temperature measurements of emitter with continuum radiation like particle streams, sooting flames

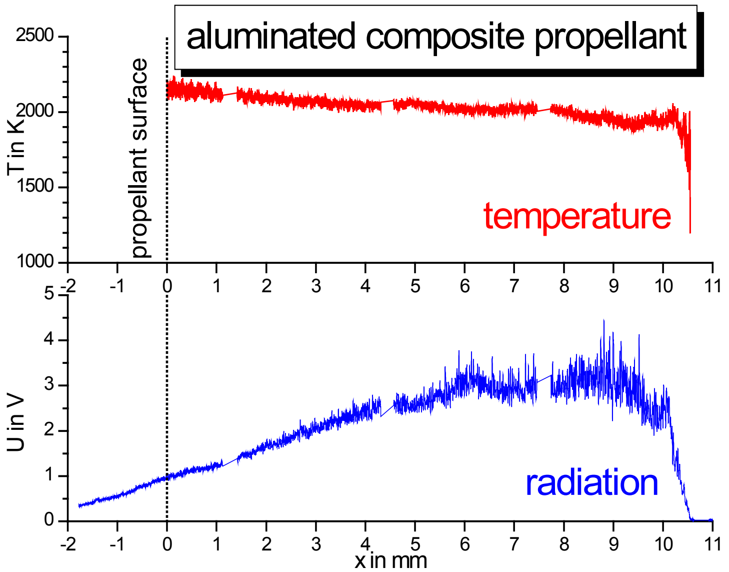
Si/Ge-sandwich detector with high sensitivity

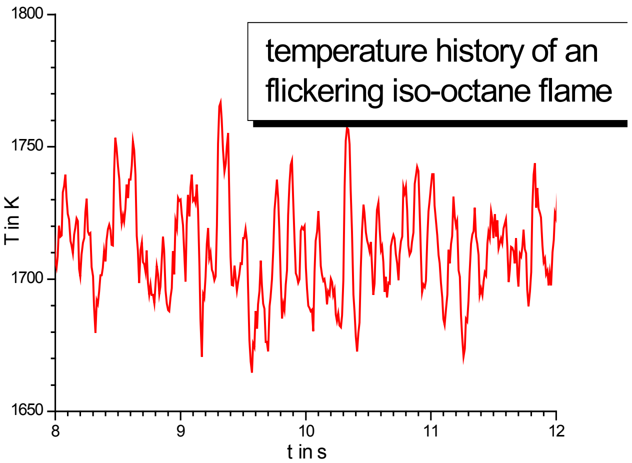
Nominal wavelength: 0.95 / 1.1 µm

Scan rate: >100 kHz

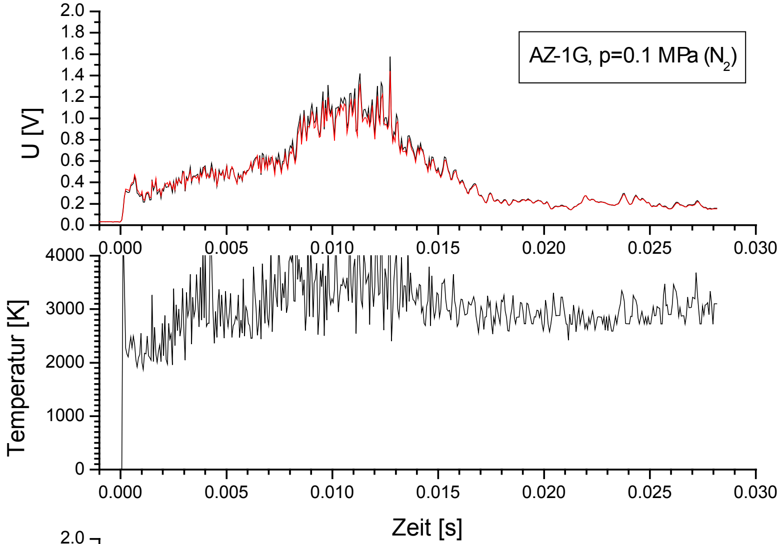
Quantitative calibration possible

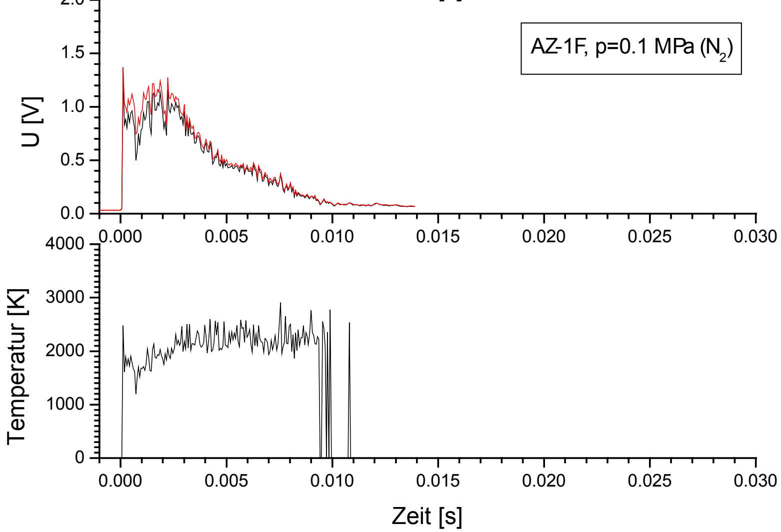
$$T = \frac{c_2\left(\frac{1}{\lambda_2} - \frac{1}{\lambda_1}\right)}{\ln\left(\frac{\varepsilon(\lambda_2)}{\varepsilon(\lambda_1)}\frac{L(\lambda_1)}{L(\lambda_2)}\left(\frac{\lambda_1}{\lambda_2}\right)^5\right)}$$





2 Colour Pyrometer: Primer Characterisation

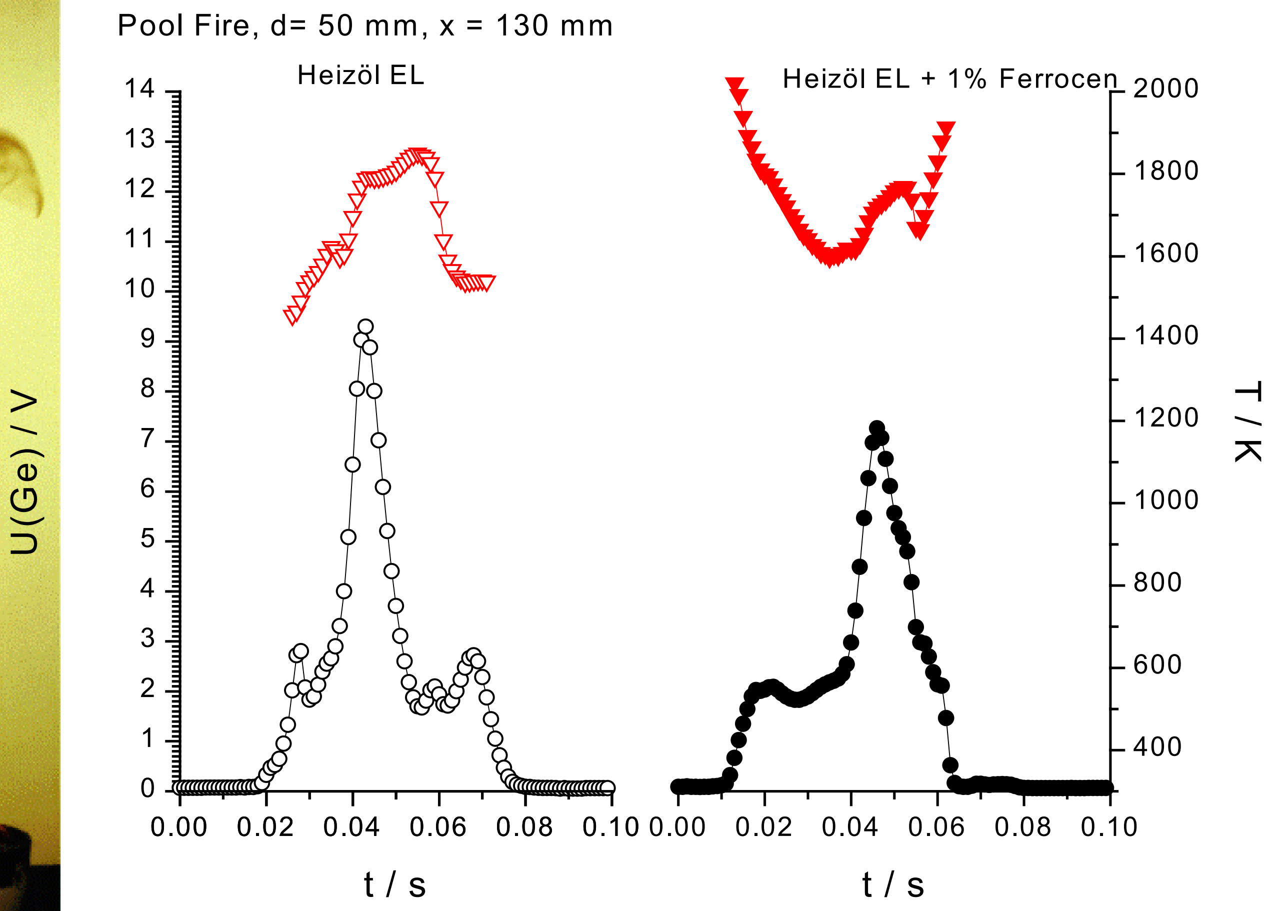




Ti-Particle
x_{50}=25µm

ultra fine
Ti-Particle

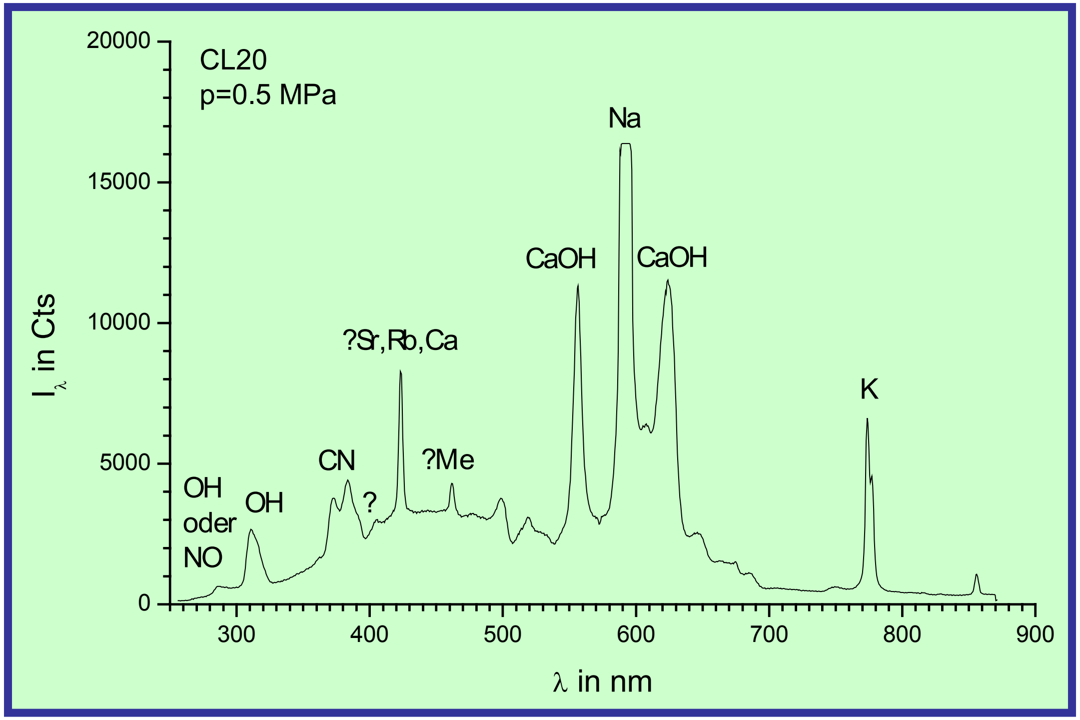
2 colour pyrometer: Soot reduction with Ferrocene (Temperature distribution in flame balls)



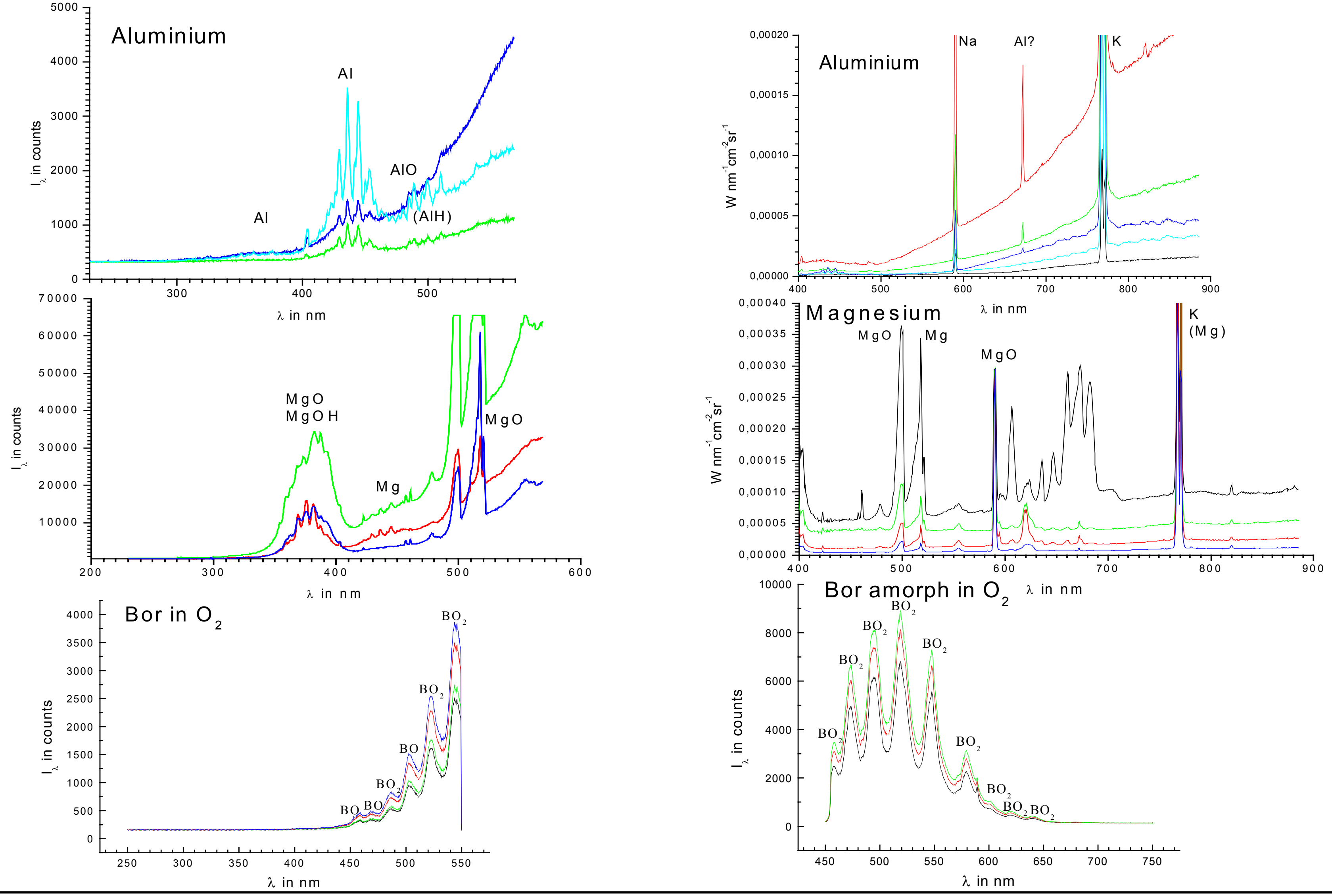
UV/Vis-Spectrometer (OMA)

ORIEL

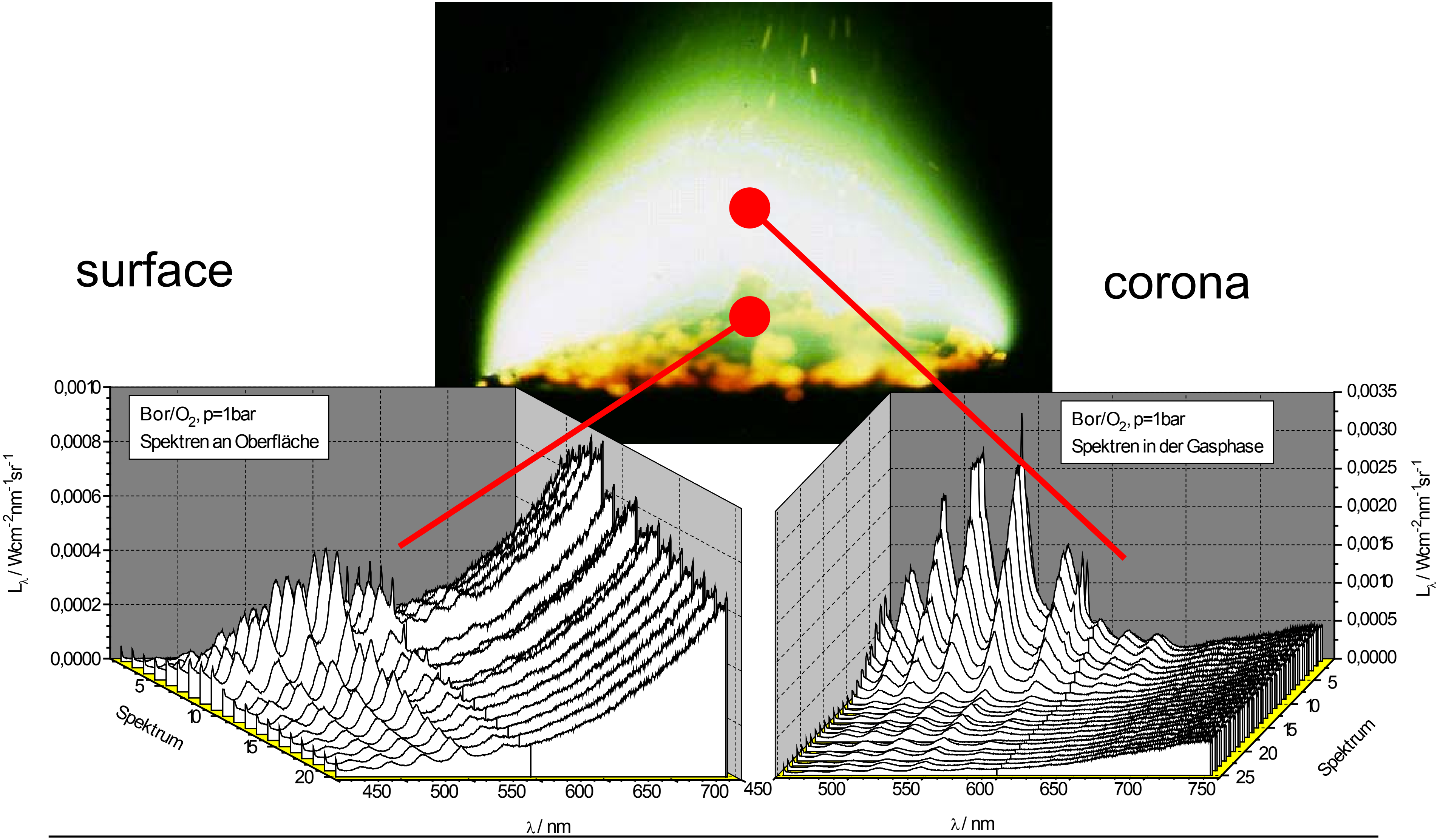
- Grating spectrometer
- Spectral range: 200 – 11000 nm
- Variable Grating: 300, 600, 2400 nm
- Detector: CCD 1024 Elements
- Wavelength accuracy: ±0,1 nm
- Resolution: <0.1 nm
- Scattering light: < 0,1 %
- Monitoring rate:
  max. 100 Spectra/s



UV/Vis-Spectra of Burning Metalls



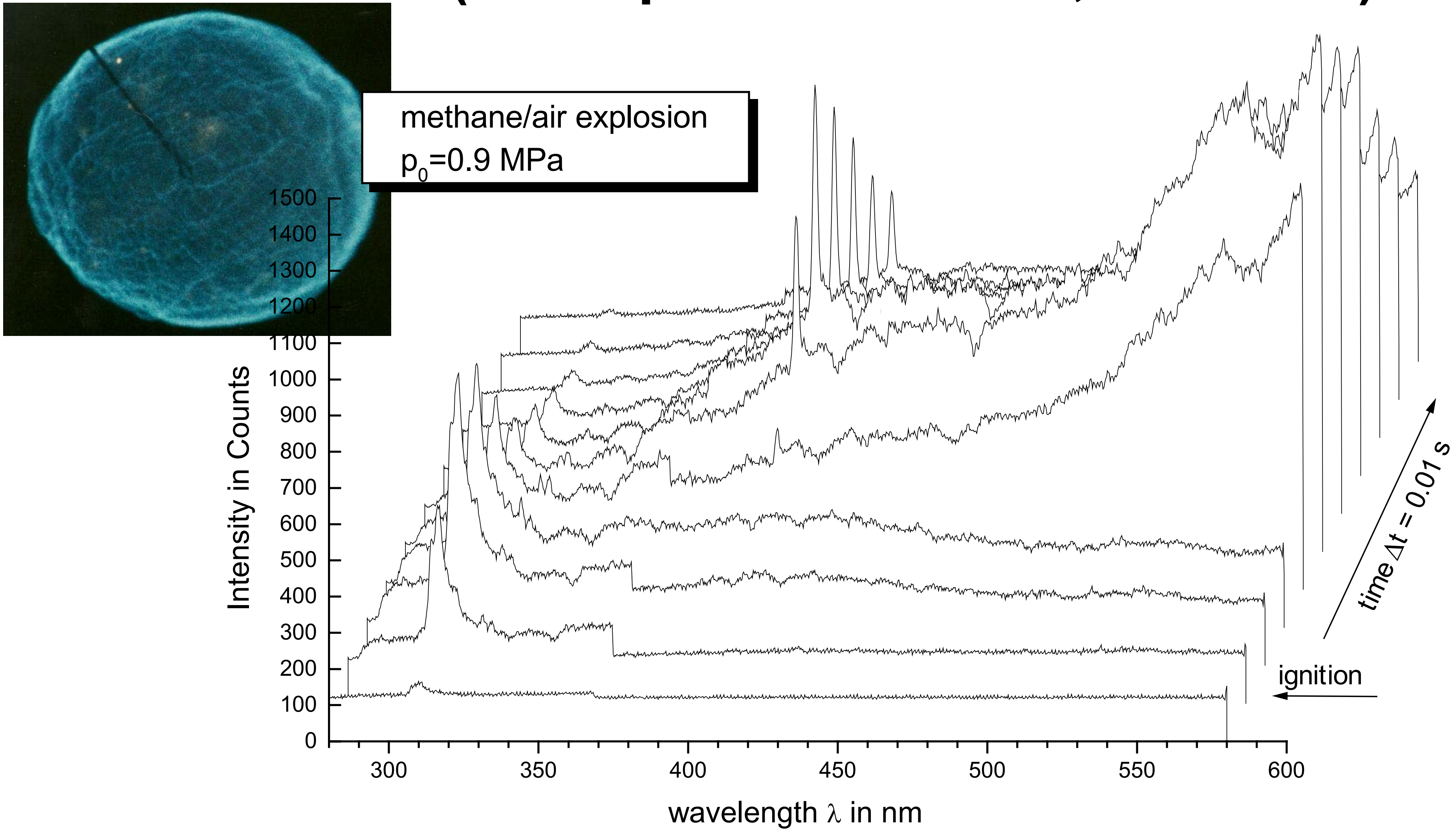
Visible Spectra of Boron in Oxygen



surface

corona

Series of UV-spectra during a gas explosion in an window bomb (initial pressure 1 MPa, Δt=0.01 s)



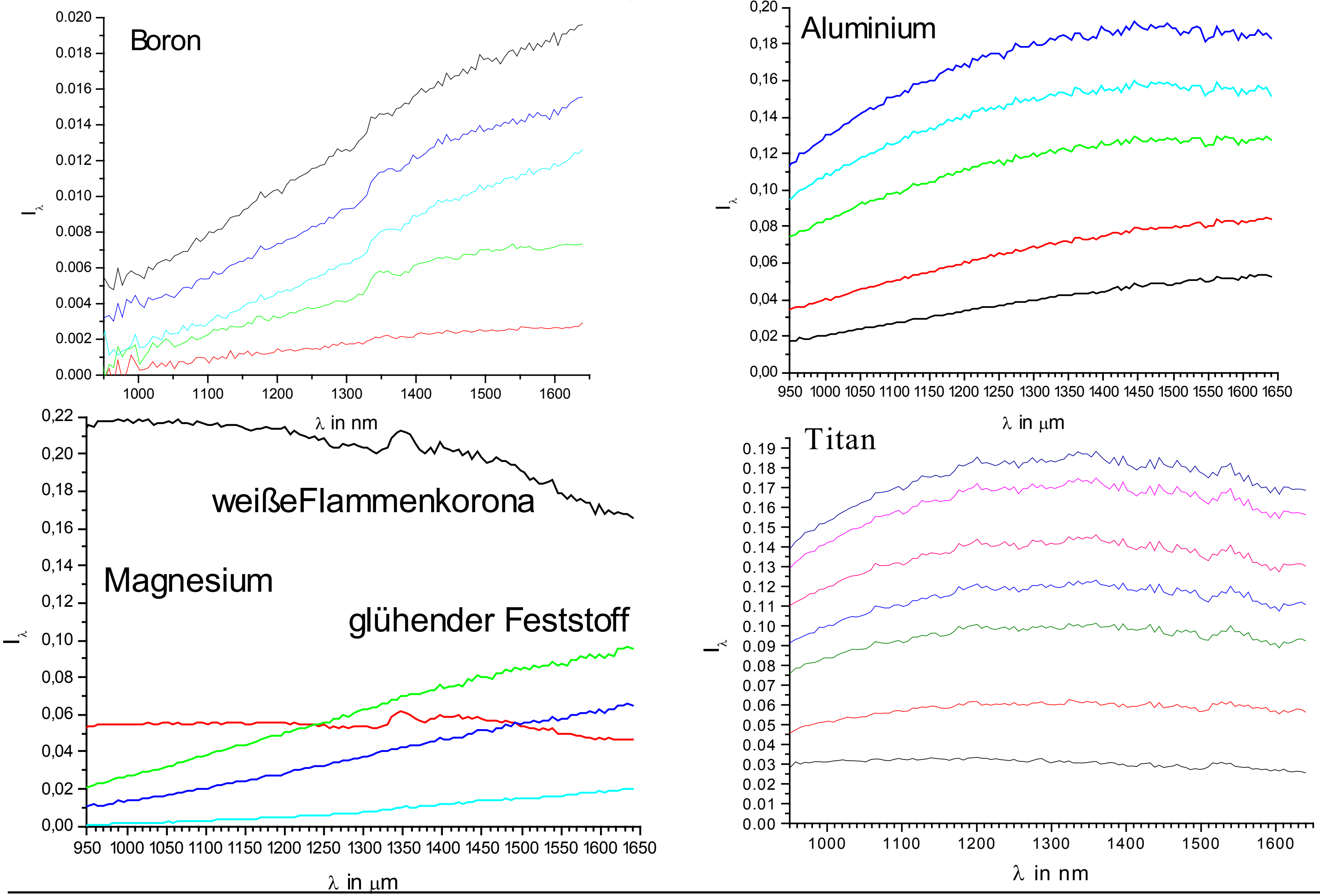
methane/air explosion
p_0=0.9 MPa

HGS - NIR-Spectrometer (Hot Gas Sensor)

Co-operation of ICT/ Zeiss Jena

- o Online spectrometer with focus of flame analysis
- o grating spectrometer based on Zeiss MCS511
- o Grating: 179 lines/mm
- o Diode array:
  128 element InGaAs diodes
- o Spectral range:
  0,9 – 1,7μm
- o Monitoring rate:
  max. 300 Spectra/s
- o Online mode to determine
  - ▪Temperature
  - ▪ water
  - ▪ soot

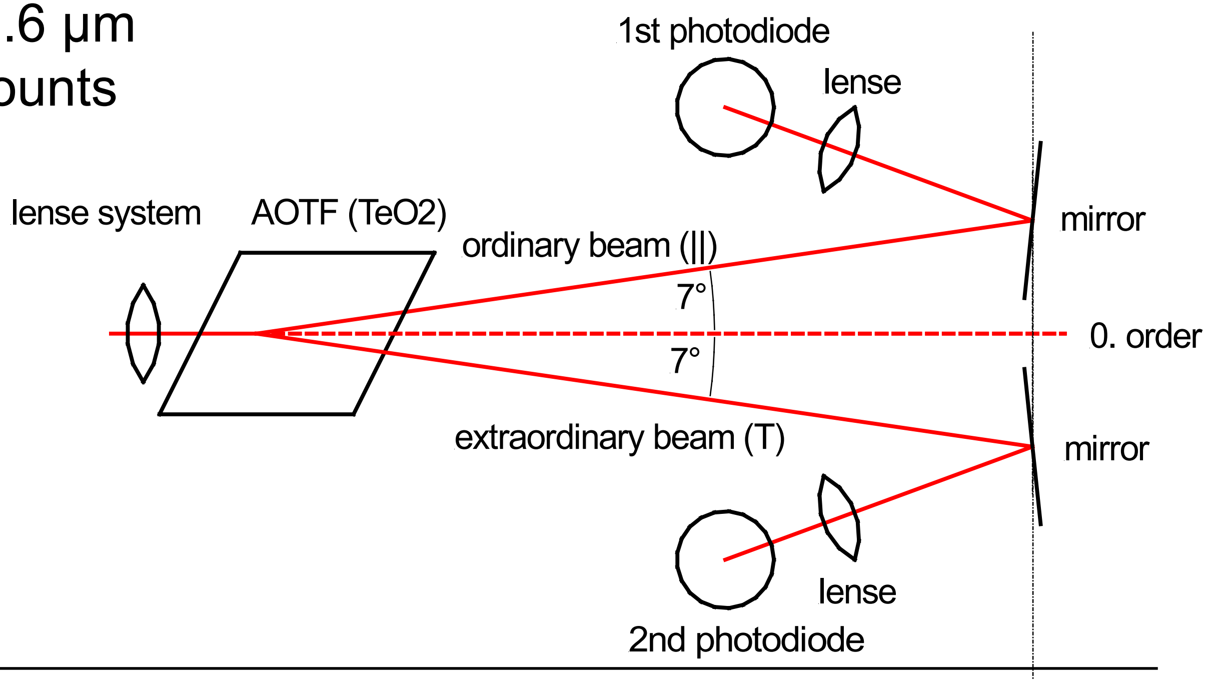
NIR-Spectra of Burning Metalls



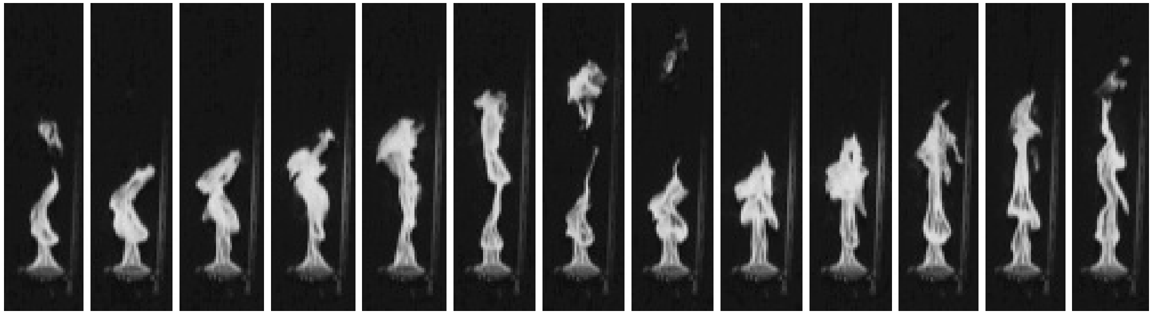
AOTF- NIR emission spectrometer

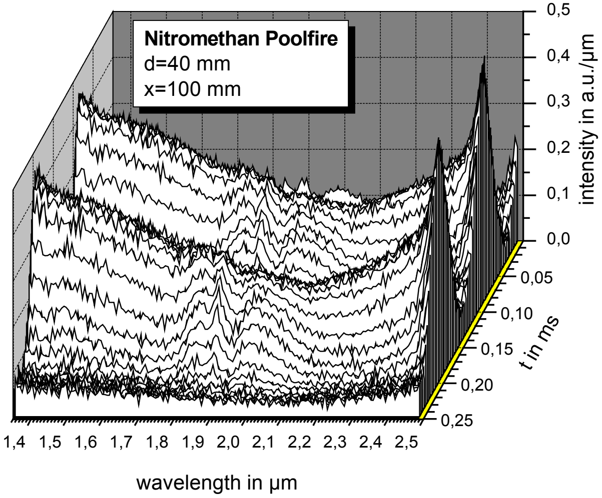
Devellopped at Fraunhofer ICT:

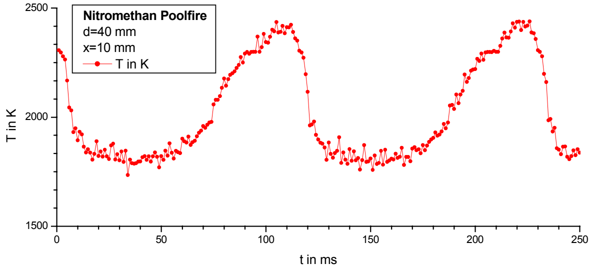
- Principle: TeO$_2$ Acousto Optical Tuneable Filter crystal becomes birefringent for a small wavelength interval when an acoustic wave of adequate frequency is transduced
- 1st order ordinary beam (parallel polarized) and 1st order extraordinary beam (perpendicular polarized)
- 2 thermoelectrical cooled InGaAs photodiodes
- Spectral range: 1.25 – 2.6 µm
- maximum scan rate amounts to about 5 µs per pixel
- Monitoring rate: max. 1000 Spectra/s
- Resolution: <7 nm

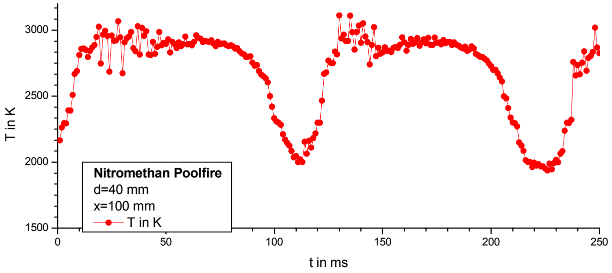


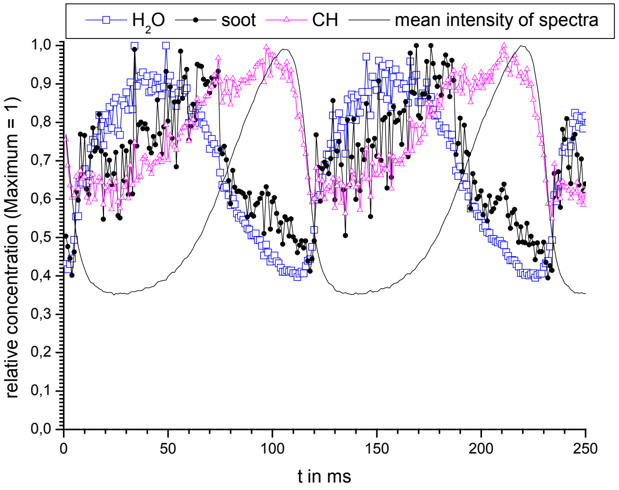
Nitromethane Pool Fire – Fit on AOTF-NIR-Data

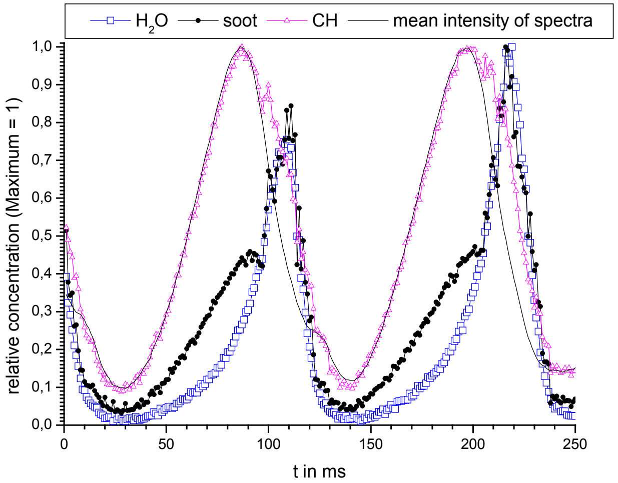


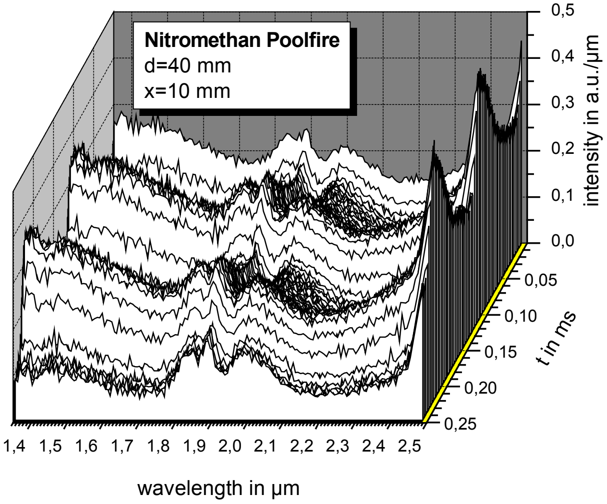












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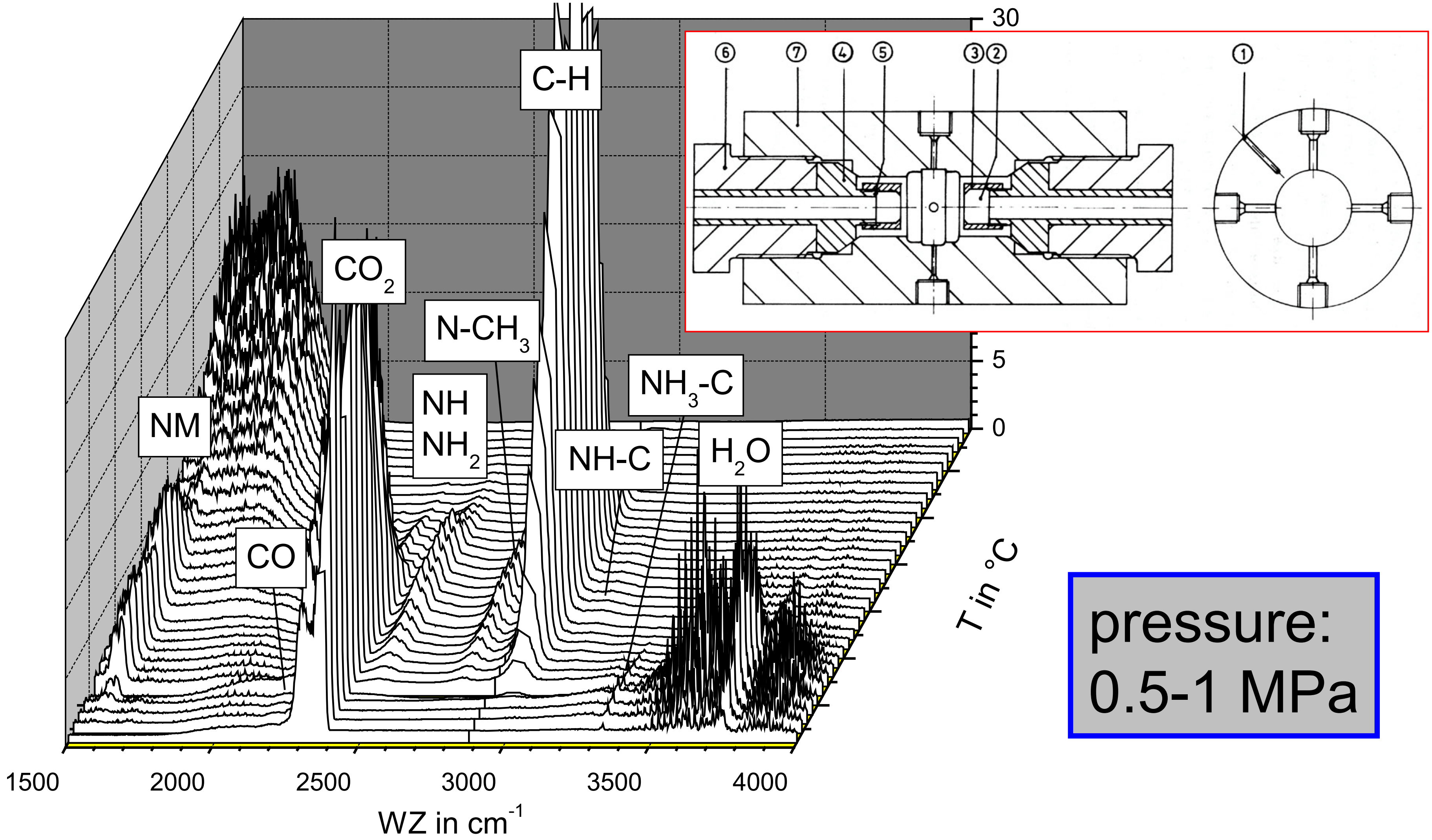
Portable FTIR-Spectrometer

MIDAC M 240-C

Michelson interferometer

Mirrow velocity:	1.25 cm/s
Spectral range:	600 - 4000 cm^{-1}
	2,5 - 16,6 µm
Accuracy:	$>$0,01 cm^{-1}
Resolution:	0,5 cm^{-1} (0,3 nm)
Detector:	MCT (LN_2 cooled)

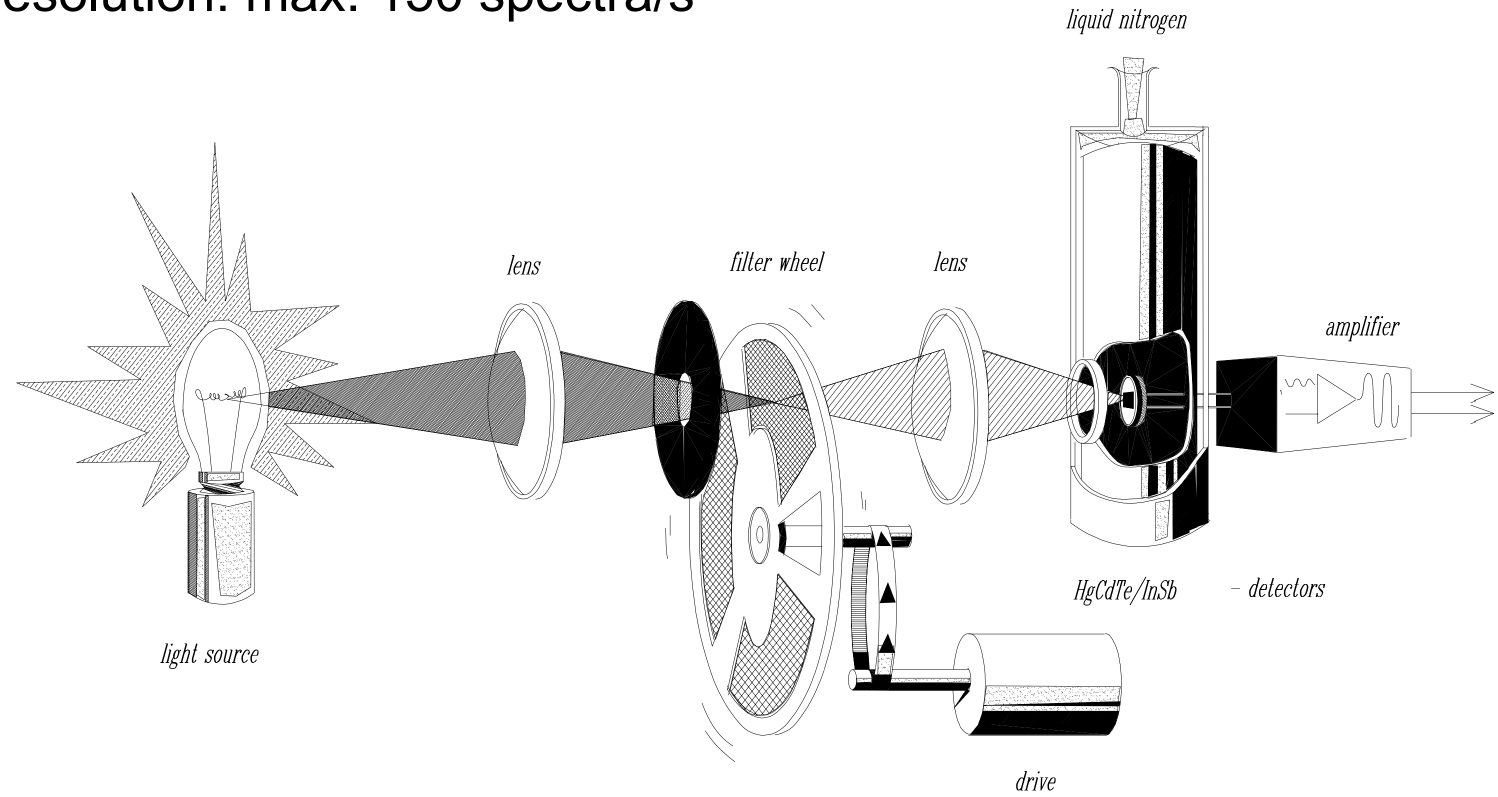
Evaporation and degregation of a nitromethane



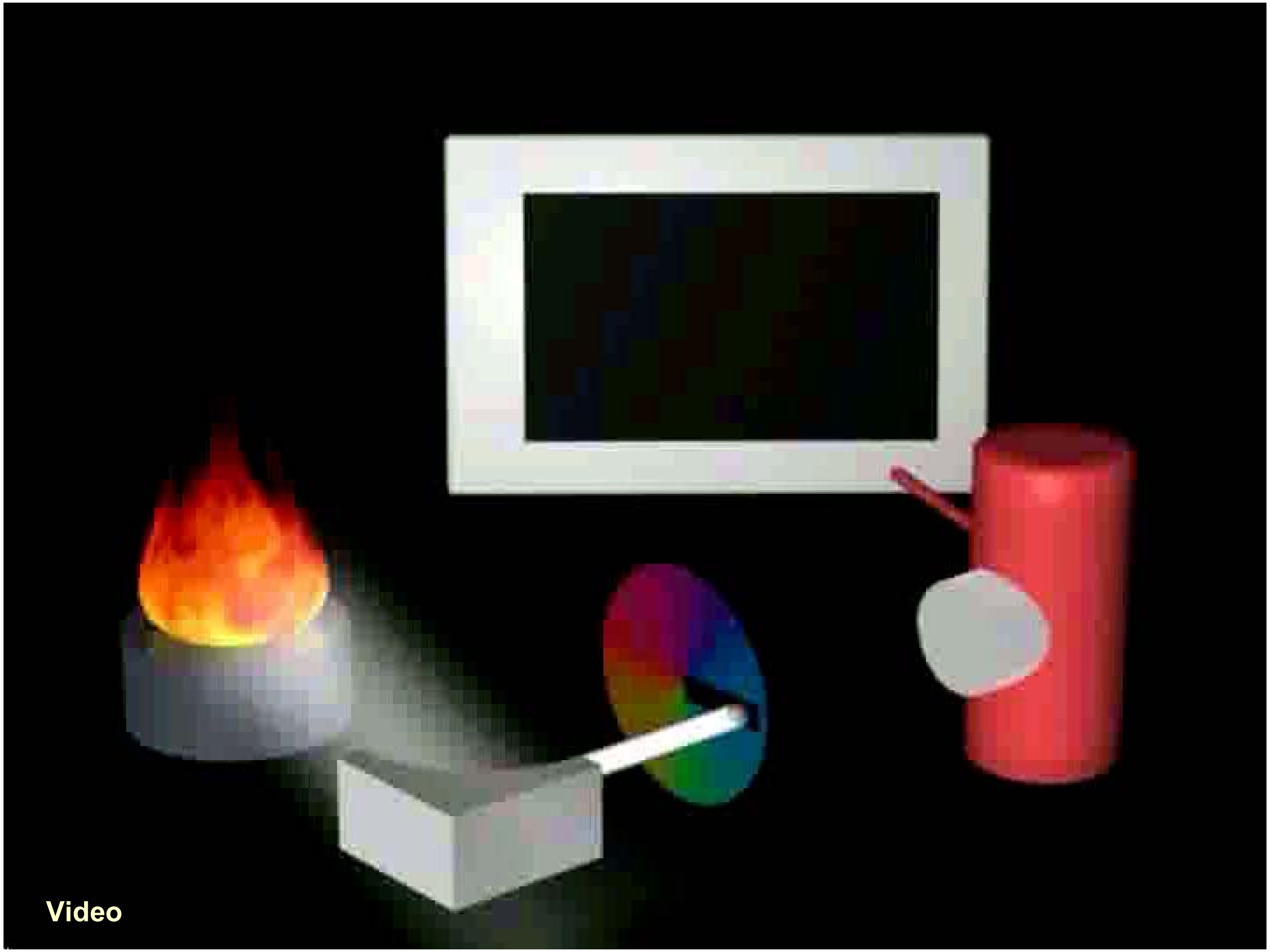
pressure:
0.5-1 MPa

IR - Filter Wheel Spectrometer

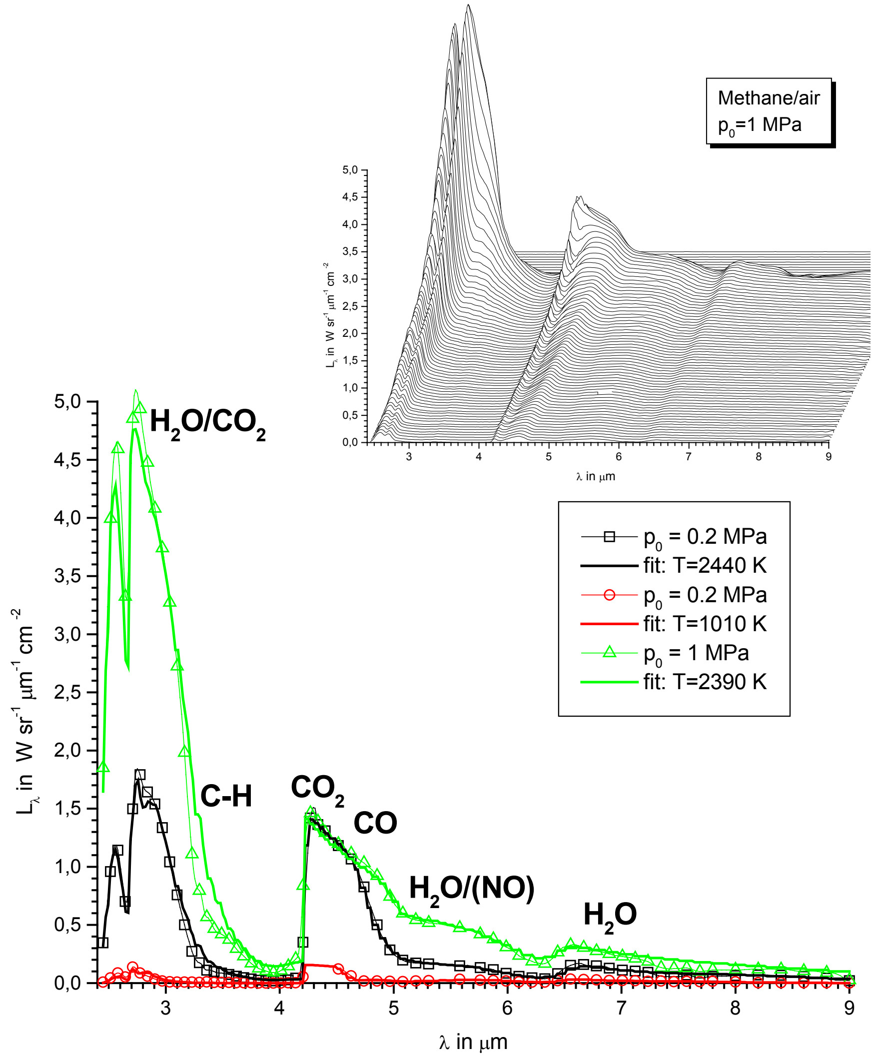
- ICT development (A. Blanc) for fast IR flame and rocket plume spectroscopy under robust conditions
- Wavelength range: 2.4 - 14 µm, resolution 2%
- LN2 cooled HgCdTe/InSb-sandwich detector
- Time resolution: max. 150 spectra/s

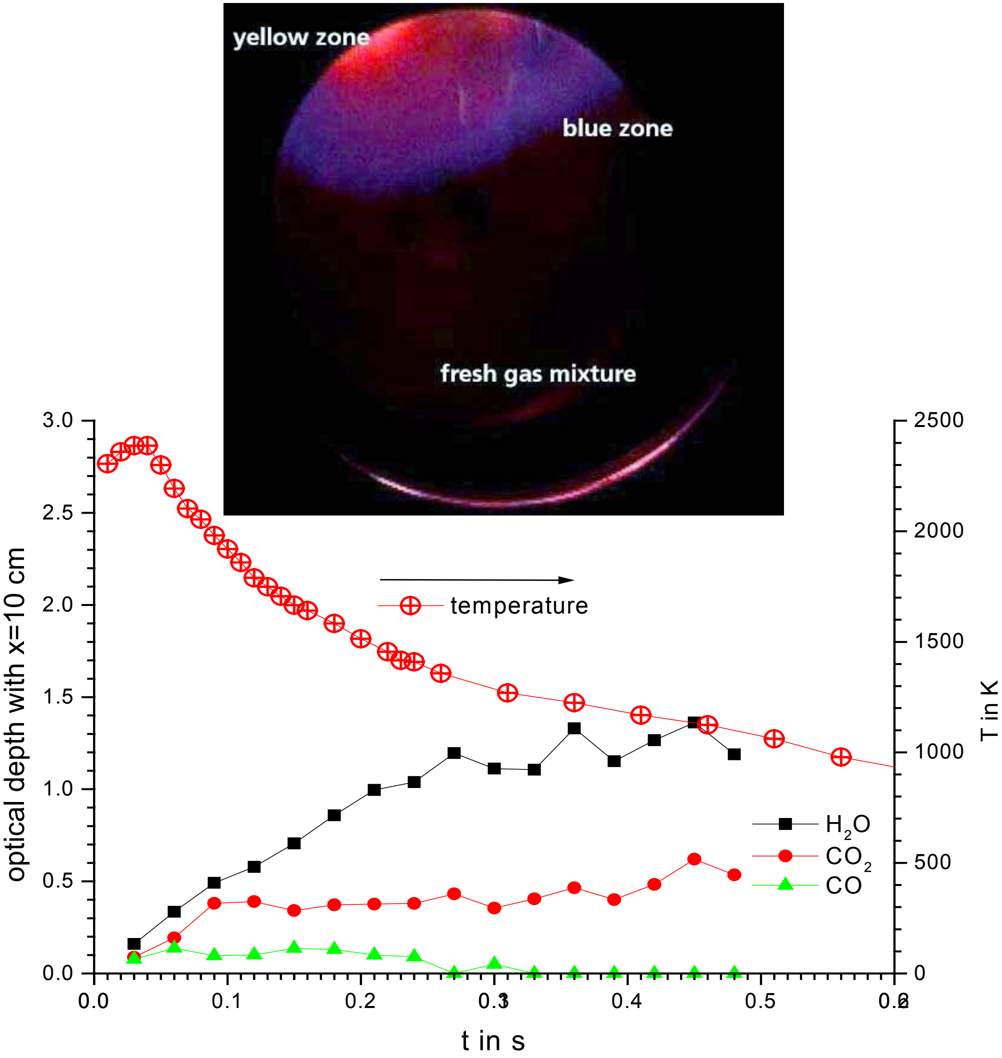


Principle of the filterwheel spectrometer



Optical depth and temperature progress of the investigated methane air deflagrations at 1 MPa





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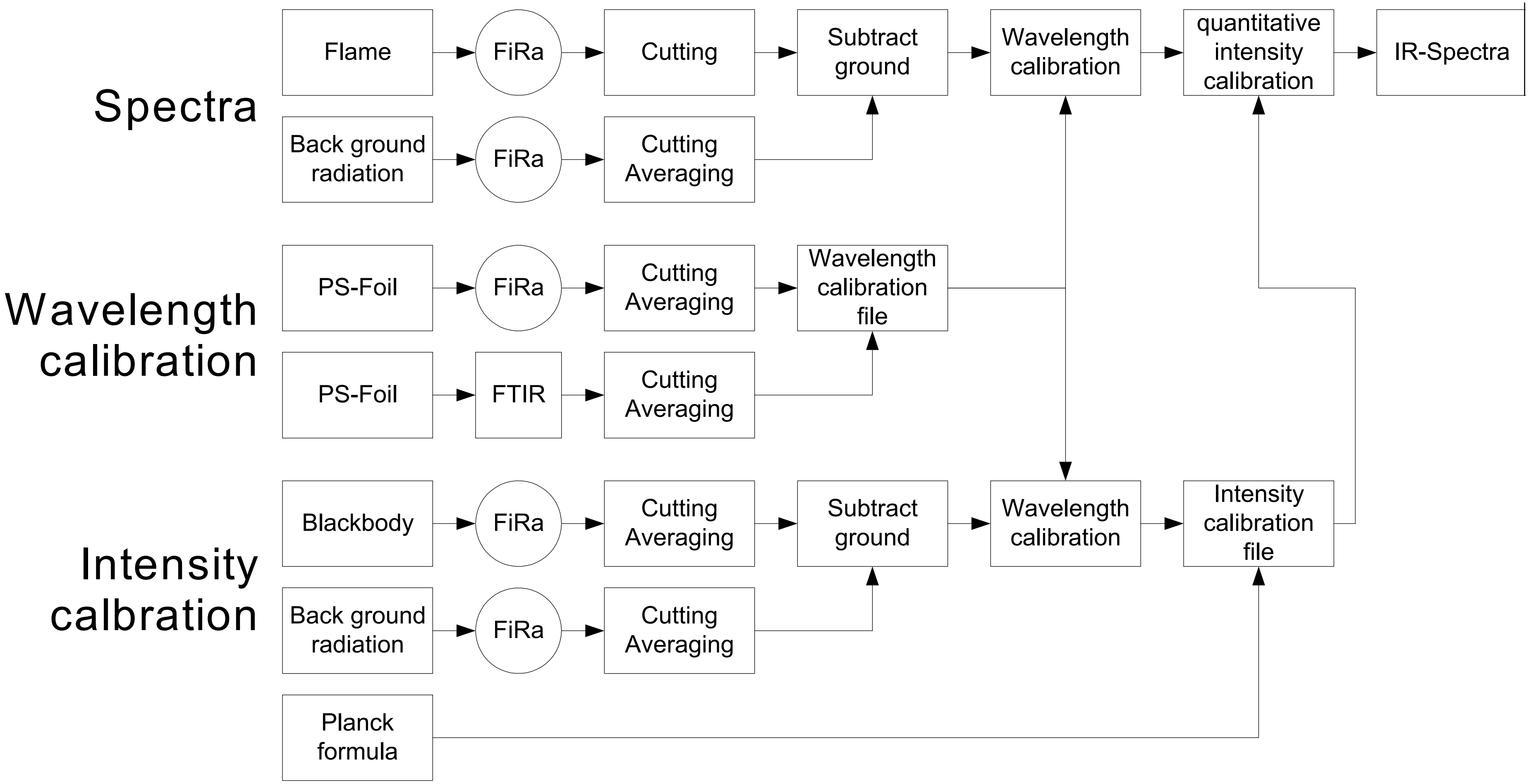
Calibration Procedure



Spectra

Flame → FiRa → Cutting → Subtract ground → Wavelength calibration → quantitative intensity calibration → IR-Spectra

Back ground radiation → FiRa → Cutting Averaging → Subtract ground

Wavelength calibration

PS-Foil → FiRa → Cutting Averaging → Wavelength calibration file

PS-Foil → FTIR → Cutting Averaging → Wavelength calibration file

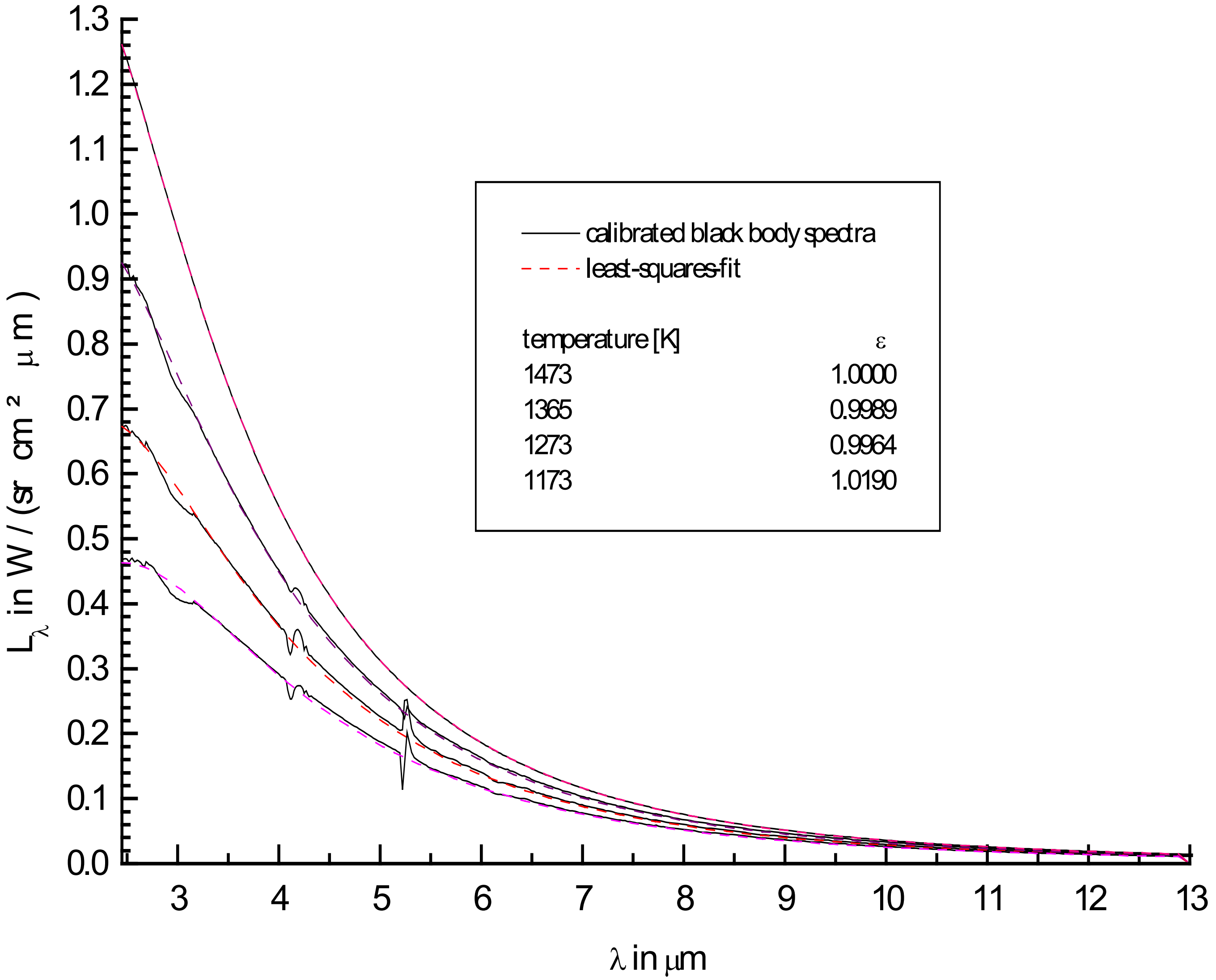
Intensity calbration

Blackbody → FiRa → Cutting Averaging → Subtract ground → Wavelength calibration → Intensity calibration file

Back ground radiation → FiRa → Cutting Averaging → Subtract ground

Planck formula → Intensity calibration file

Quantitative calibration at a black body



temperature [K]	ε
1473	1.0000
1365	0.9989
1273	0.9964
1173	1.0190

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Spectra modelling
and
data analysis

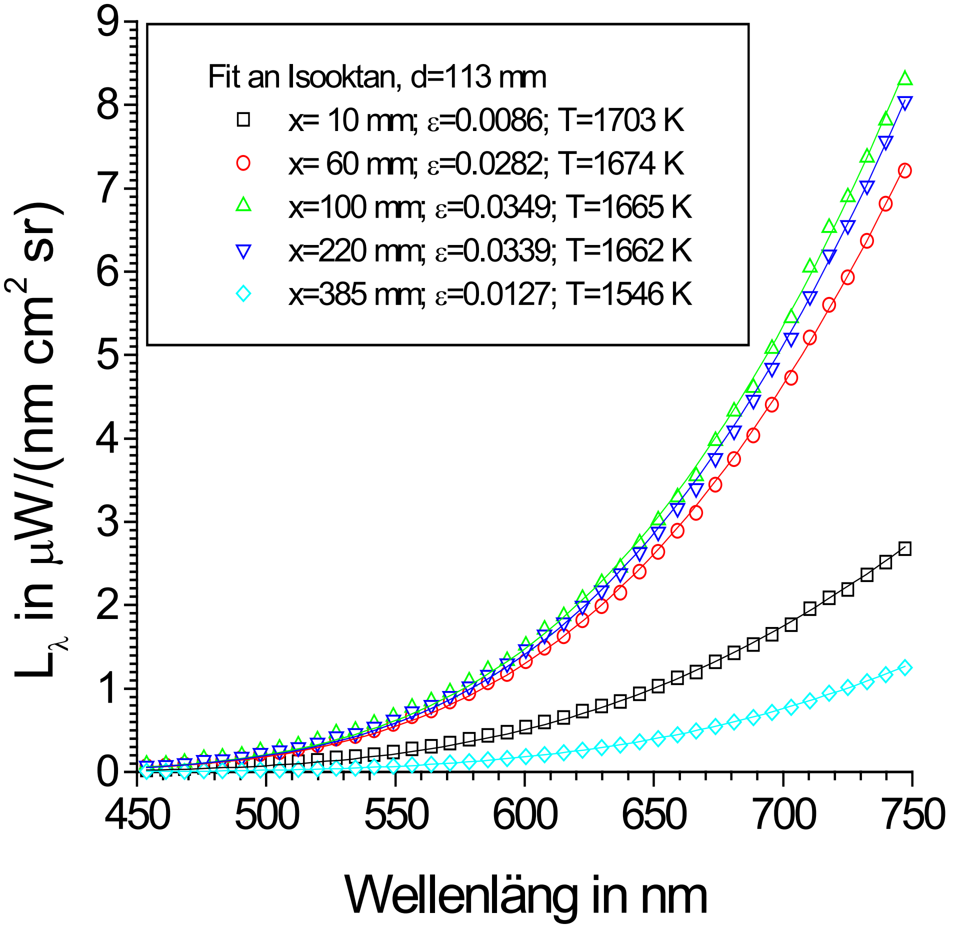
Continuum Fit Method

Least-Squares-Fit on Plancks blackbody radiation profile to quantitative calibrated emission spectra

$$L_{\lambda S}(\lambda,T)=\varepsilon\,\frac{c_1}{\lambda^5\left(\exp\left(\frac{c_2}{\lambda T}\right)-1\right)}\,\frac{1}{\Omega_0}$$

$$c_1=2hc^2=1.191\times10^{-16}\,\mathrm{Wm}^2$$

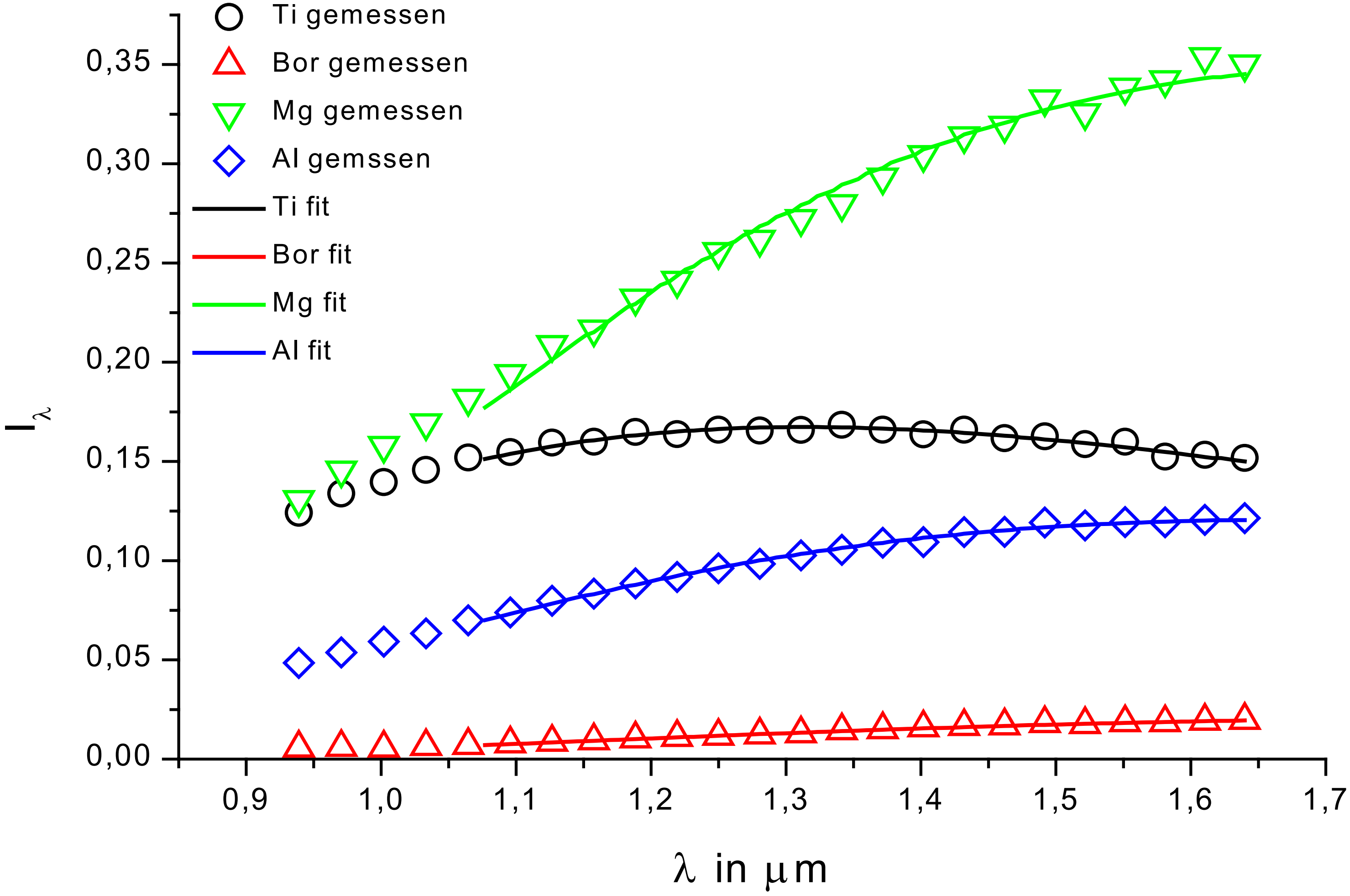
$$c_2=\frac{hc}{k}=1.439\times10^{-2}\,\mathrm{mK}$$



Fit parameter:

- emission degree ε or ε(λ)
- temperature T

NIR-Greybody Fit for Temperature Determination of Pyrotechnics



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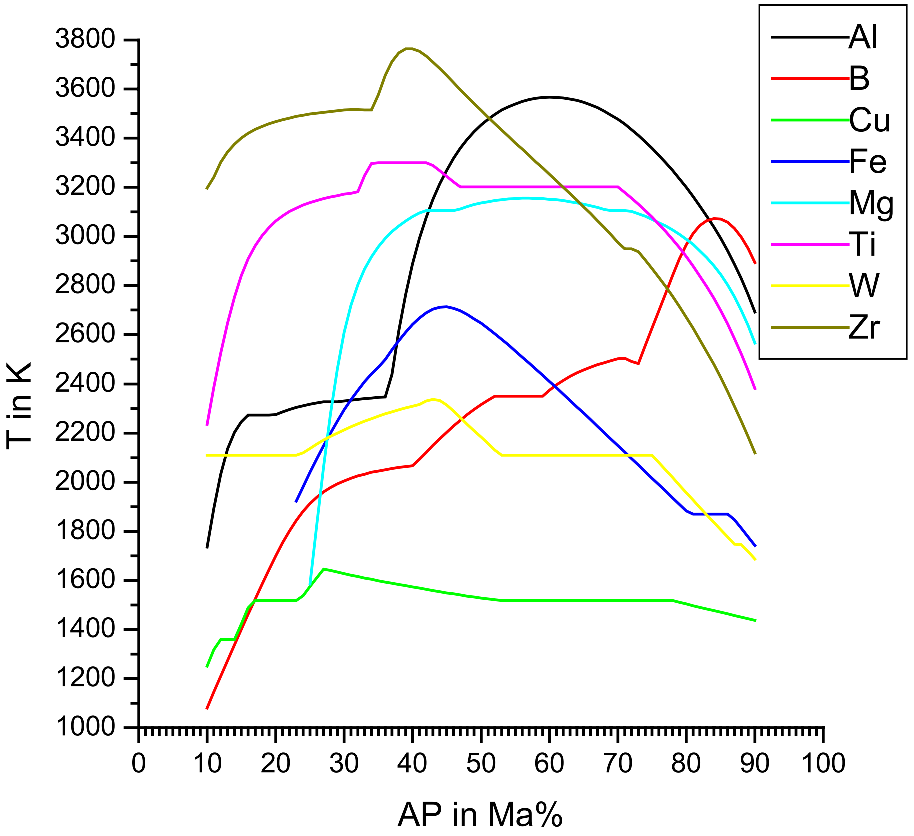
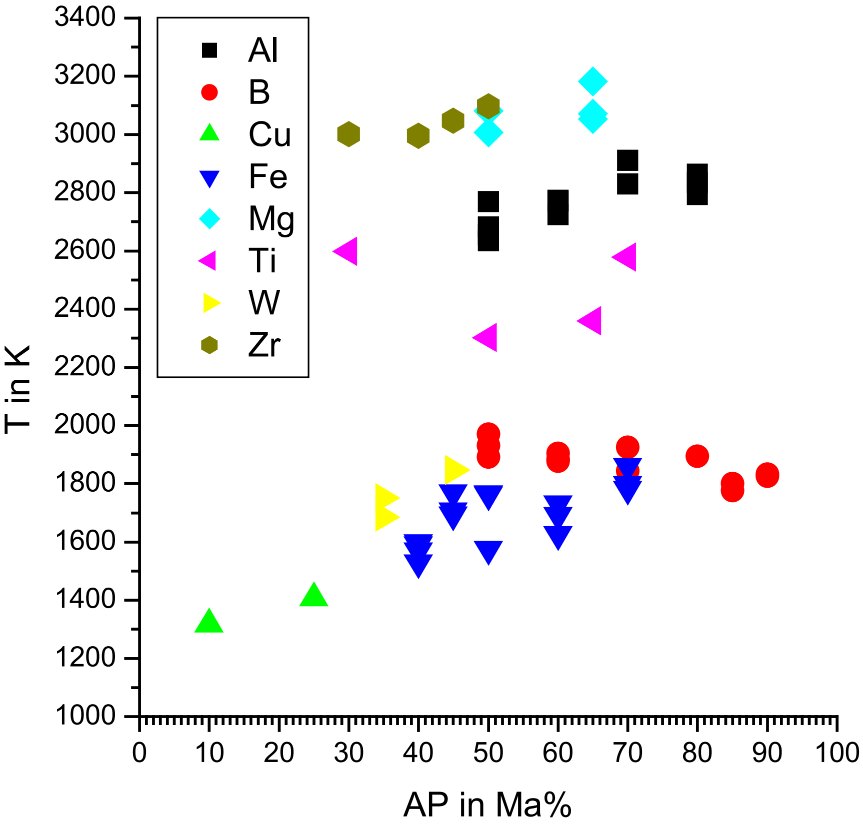
NIR-Spectroscopy to Characterize Temperature of AP/Metal Mixtures



Temperatures calculated with ICT-Code



Temperatures measured with HGS

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Modelling Diatomic Molecules

The determination of rotational and vibrational temperatures of various diatomic molecules from UV/VIS emission spectra is based on the calculation of line intensities and profiles.

intensity of a spectral line: $I_{em} = N_n h c \nu_{nm} A_{nm}$

Assumptions: thermal equilibrium
Born-Oppenheimer approximation
explicit expression for Einstein coefficients

$$I_{em} = C \cdot q_{j'j''} \cdot S_{j'j''} \cdot \nu^4 \cdot \exp(-E_{vib}/kT_{vib} - E_{rot}/kT_{rot})$$

Correction of self absorption: $I = \int dI = \frac{\varepsilon}{k}(1 - \exp(-kx))$

Emission spectra modelling of diatomic molecules

Electron transition: $$h\upsilon = E'_{total} - E''_{total}$$

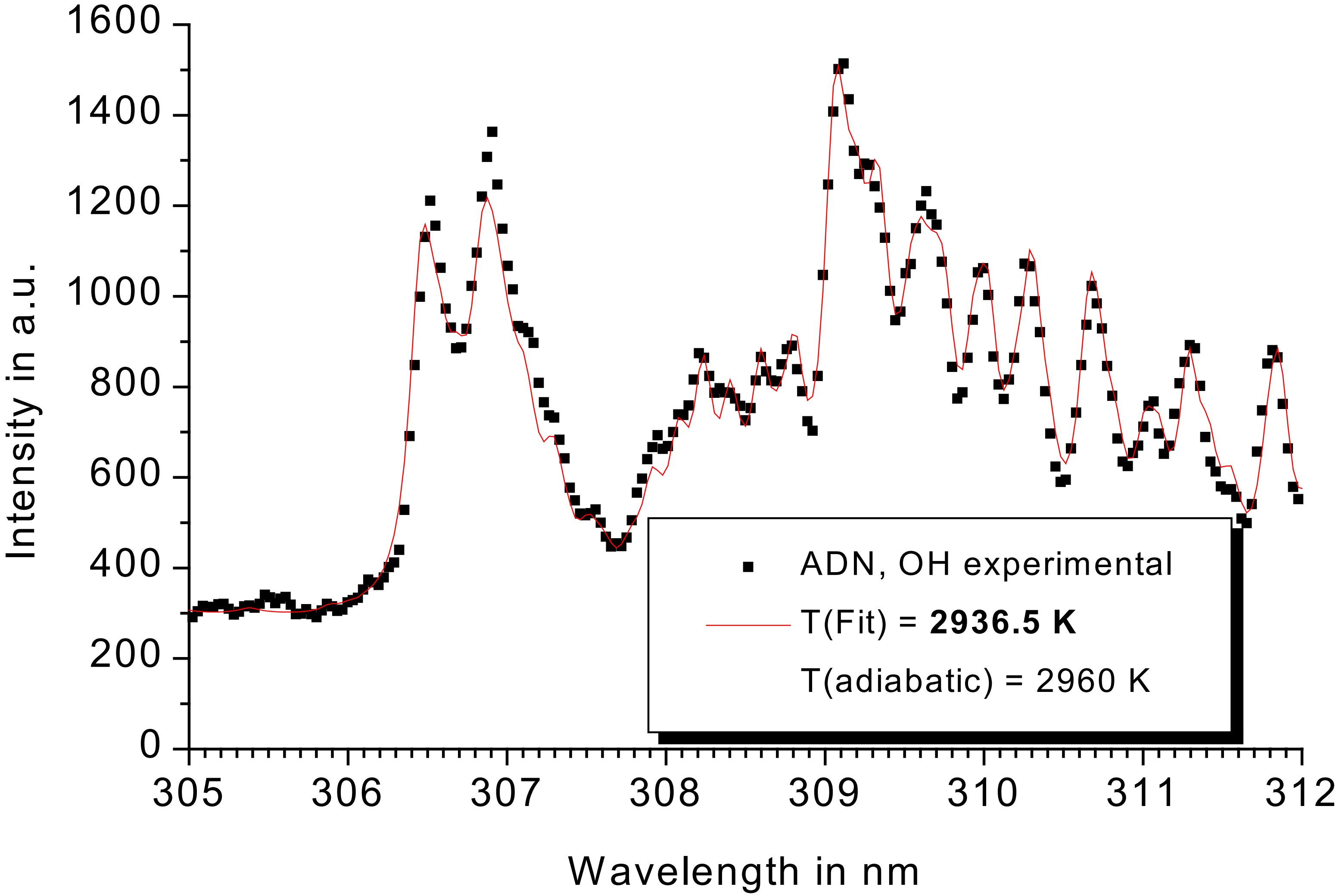
Neglecting multiplett separation, fine structure (Λ duplication) and coupling of rotation momentum

Available:

Molecule	Transition	Wavelength in nm
OH	$A_2\Sigma \leftarrow X_2\Pi$	260 - 370
C_2	$A_3\Pi \leftarrow X_3\Pi$	440 - 680
CN	$A_2\Pi \leftarrow X_2\Sigma$ $B_2\Sigma \leftarrow X_2\Sigma$	390 - 1520 360 - 460
CO^+	$A_2\Pi \leftarrow X_2\Sigma$ $B_2\Sigma \leftarrow X_2\Sigma$	310 - 630 200 - 230
CH	$A_2\Delta \leftarrow X_2\Pi$ $B_2\Sigma \leftarrow X_2\Pi$	350 - 560 360 - 500
NH	$A_3\Pi \leftarrow X_3\Sigma$	300 - 380
CO	$A_1\Pi \leftarrow X_1\Sigma$	130 - 220
O_2	$b_1\Sigma \leftarrow X_3\Sigma$	625 - 1040

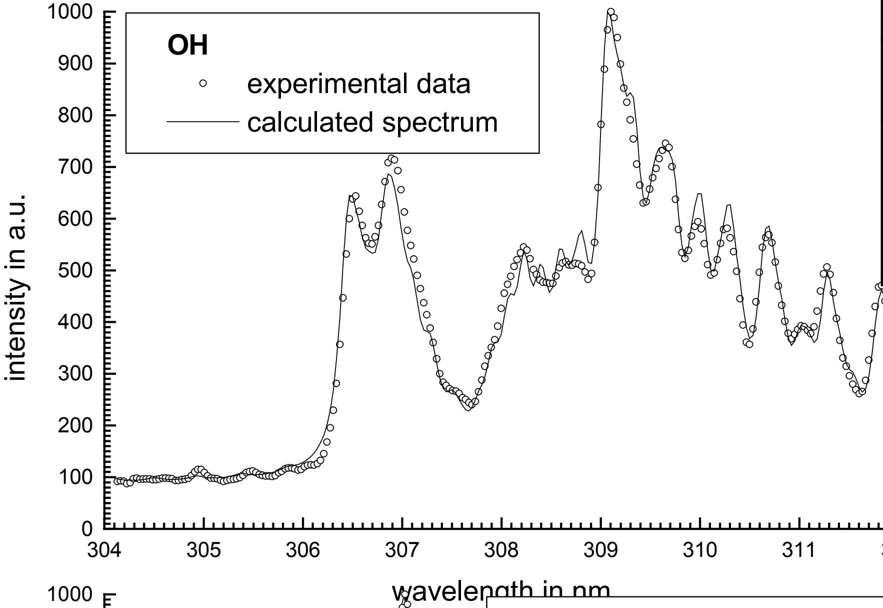
All over more than 10000 line

Temperature determination in the reaction zone at 0.5 MPa of ADN/Paraffin from OH-emission

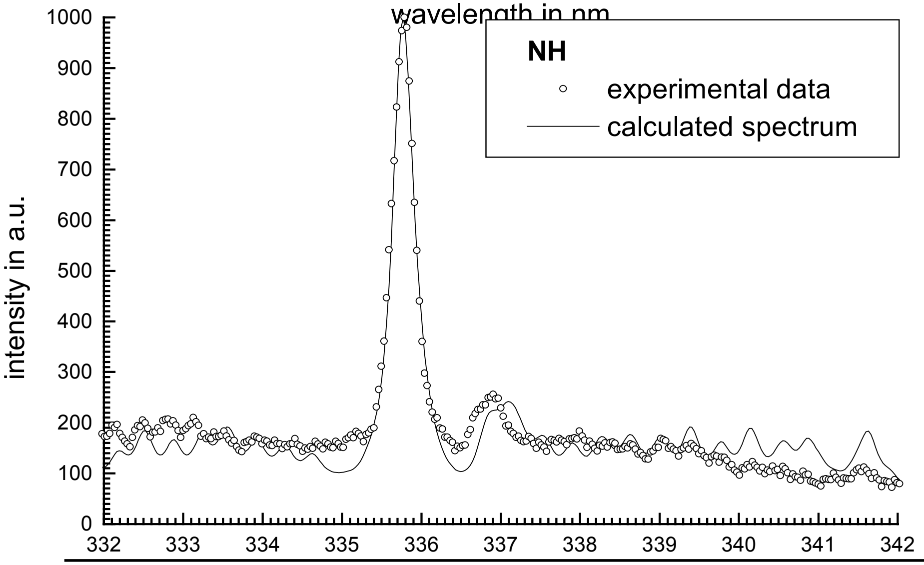


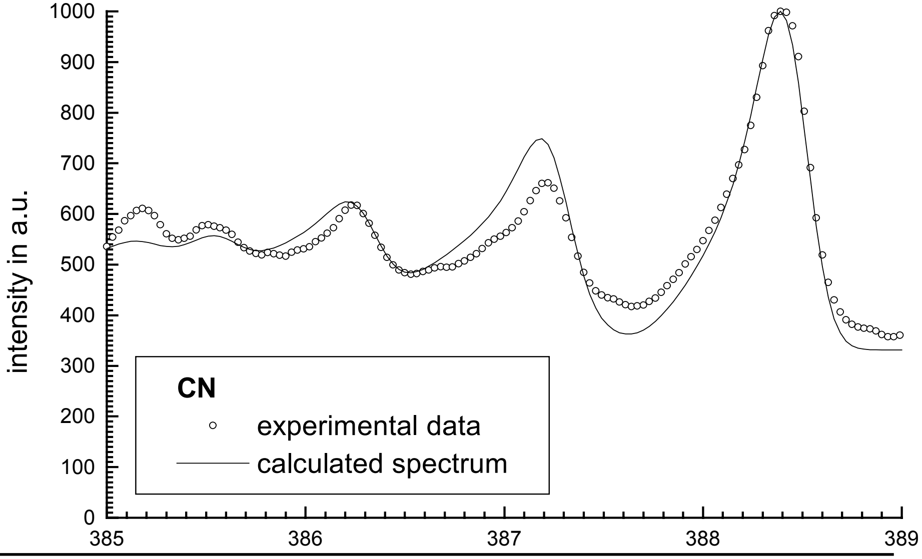
UV/Vis-spectra: Sampled and fitted

Molecule	Transition	T_{rot}	T_{vib}
OH	$X^2\Pi$ - $A^2\Sigma$	2380 K (± 120 K)	= T_{rot}
NH	$X^3\Pi$ - $A^3\Pi$	2300 K (± 170 K)	= T_{rot}
CN	$X^2\Sigma$ - $A^2\Pi$	2100 K (± 110 K)	4300 K (± 210 K)

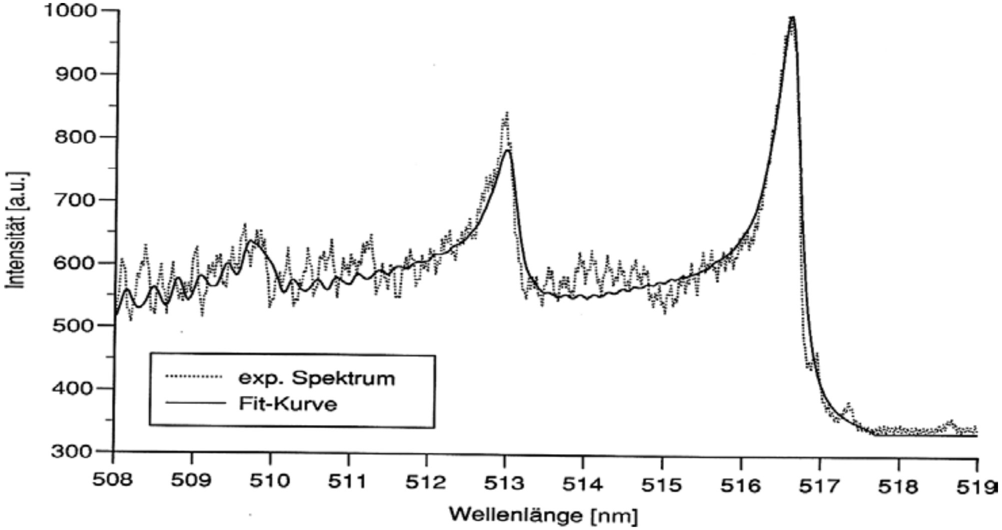


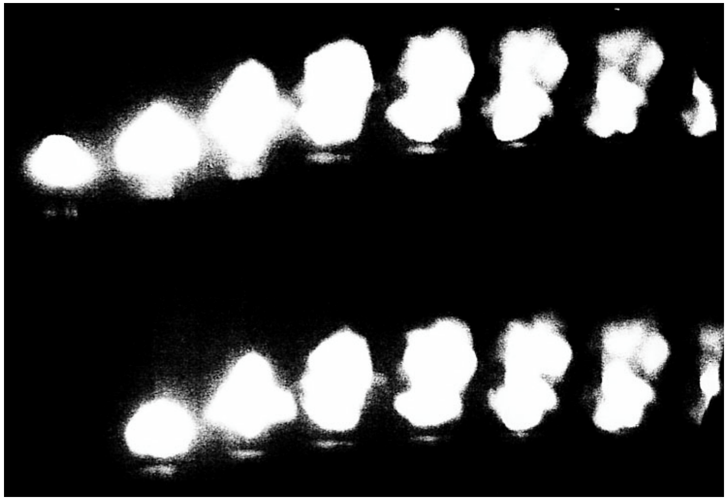
Nitromethane





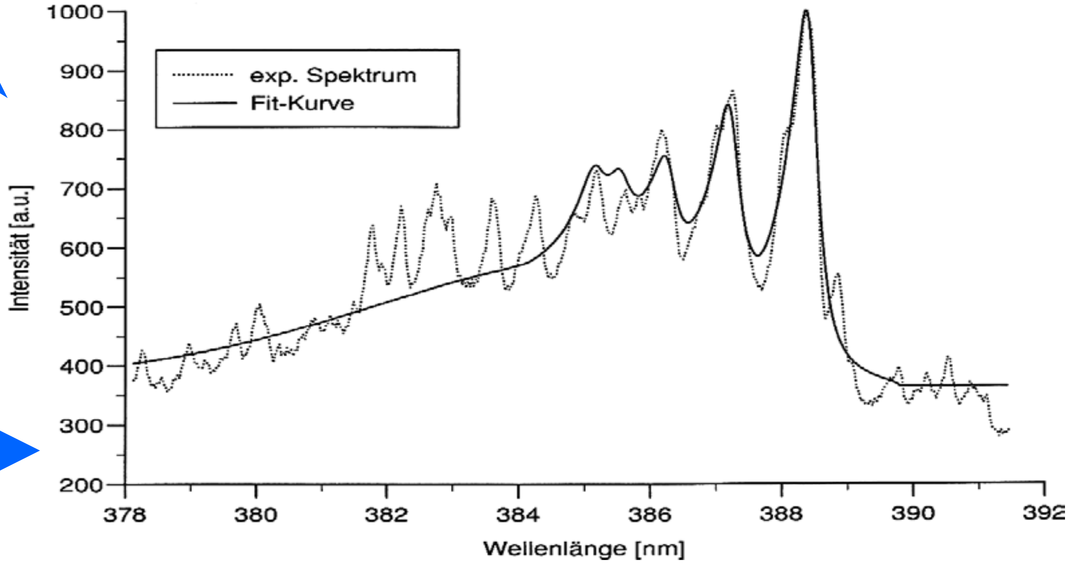
Temperature of ETC-Plasmas





isooctane plasma (C_2)
T_{rot}=4600 K
T_{vib}=8700K

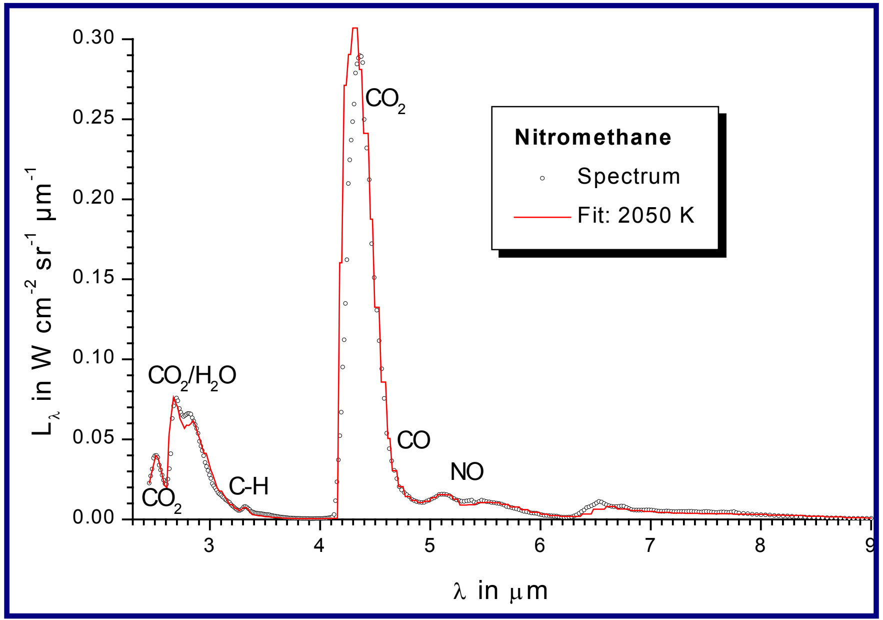
2-propanol plasma (CN)
T_{rot}=5000 K
T_{vib}=6000K



Data analysis of NIR/IR spectra (BAM)

Computer code for generation and fitting of NIR/IR spectra (1-10 µm):

- band modelling based on single line group model, Curtis-Godson-approximation and tabulated data of H_2O and CO_2
- Database: NASA-Handbook of Infrared Radiation from Combustion Gases
- inhomogeneous gas mixtures of
  - H_2O (bands at 1.3, 1.8, 2.7 and 6.2 µm)
  - CO_2 (bands at 2.7 and 4.3 µm)
  - CO (band at 4.7 µm)
  - NO (band at 5.4 µm)
  - HCl (band at 3.5 µm)
  - particles (e.g. soot)



- temperature range 300 - >3000 K
- emission or transmission calculations
- single or multi-layer model of radiation transfer
- Fitting parameter: <u>Temperature</u>, (<u>concentration * path length)</u>

Data analysis of NIR/IR spectra (BAM)

Band models allow suitable calculation of spectroscopic radiative heat transfer, therefore they use only moderate spectral resolution. High resolution:
e.g. CO_2 60000 lines; H_2O 50000 lines (HITRAN DB)

Band models use line profile, half width and statistic distribution of the lines.

Preferential: random band model with Doppler-Lorentz line profile

Per molecule type a “single line group” are used (SLG)

“Curve of Growth”: Gurtis-Godson-Approximation

The optical path is approximated using a sequence of homogeneous layers.

Assumption for emission and absorption of soot particles:

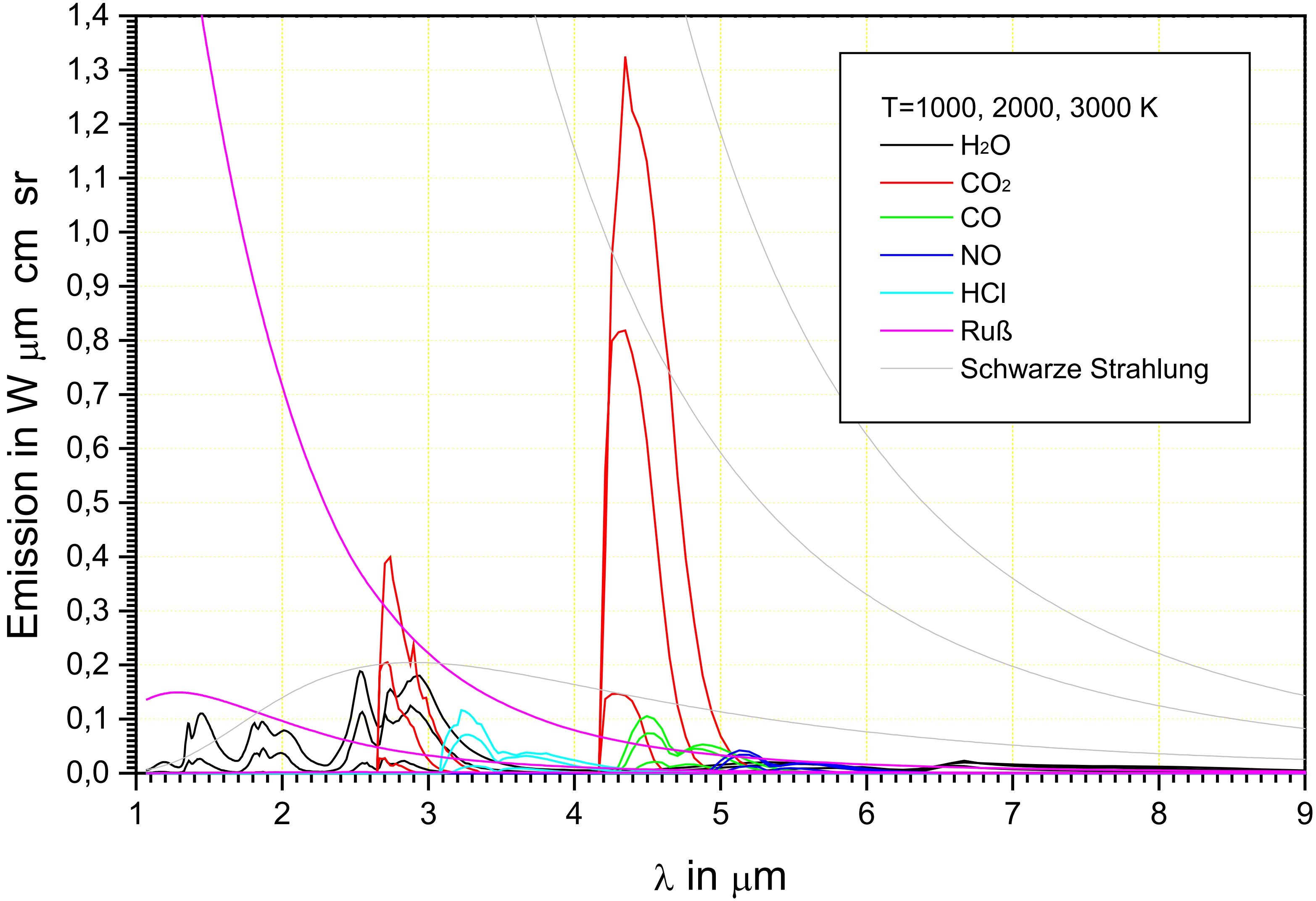
particle size << wavelength

complex refraction index (e.g. Sarofim)

Absorption koefficient of soot radiation

$$k_{soot}(\lambda) = \frac{36\pi\rho F(\lambda)}{\rho_0 \lambda}$$

BAM-Emission spectra at T=1000, 2000, 3000 K



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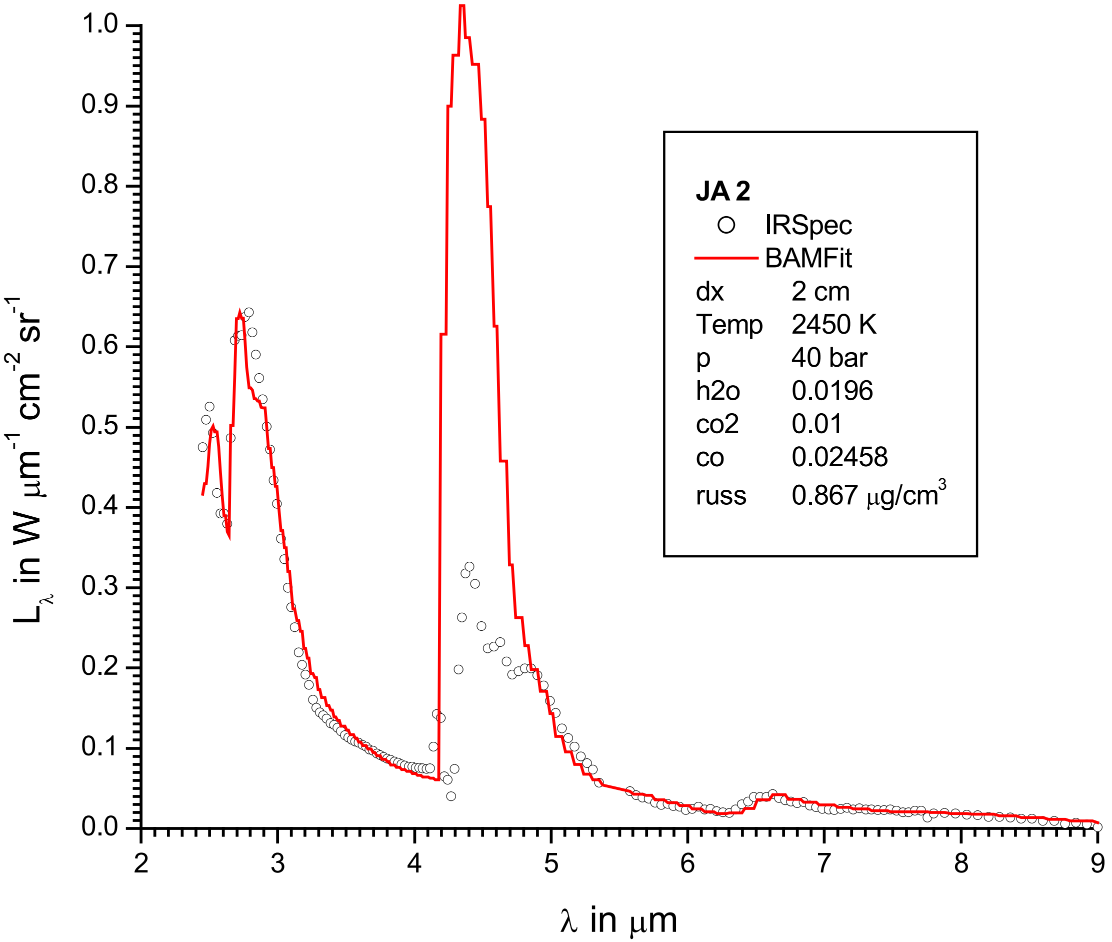
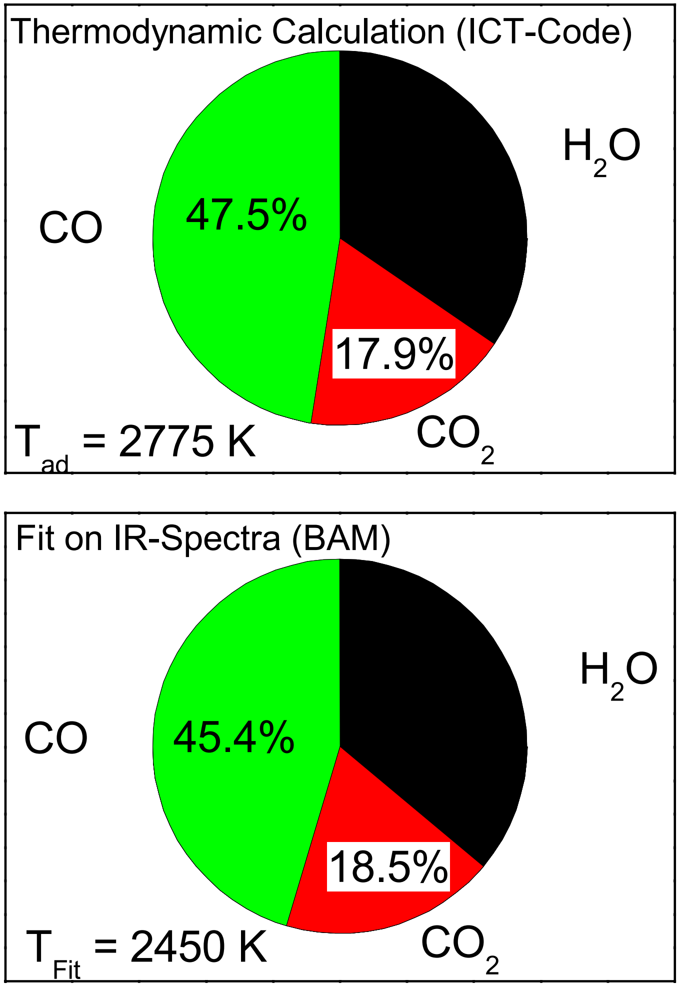
IR-Emissionsspectrum: ICT-Code versus BAM-Fit



Fraction of H_2O, CO, CO_2



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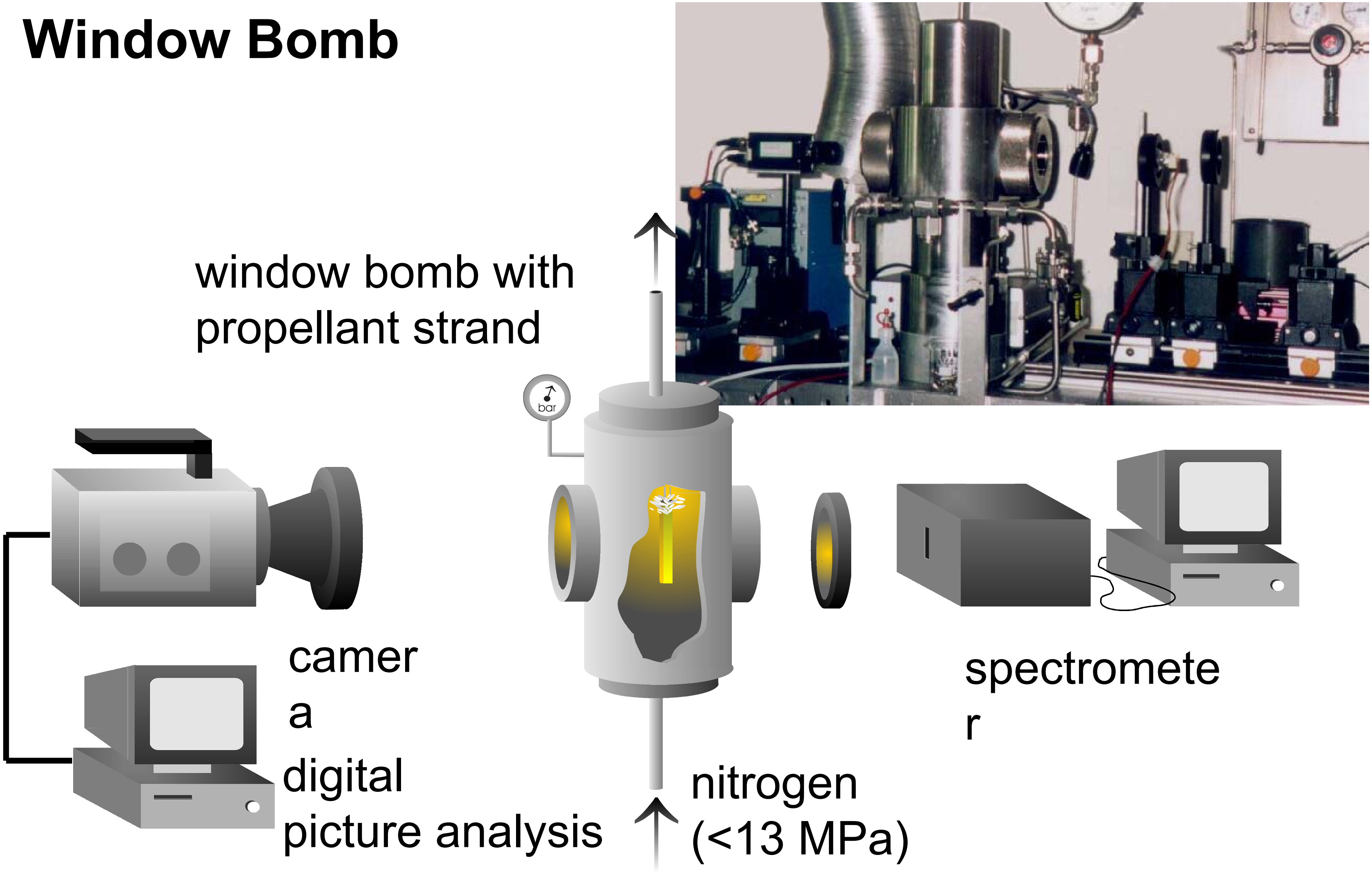
Further Examples

Window Bomb



window bomb with
propellant strand

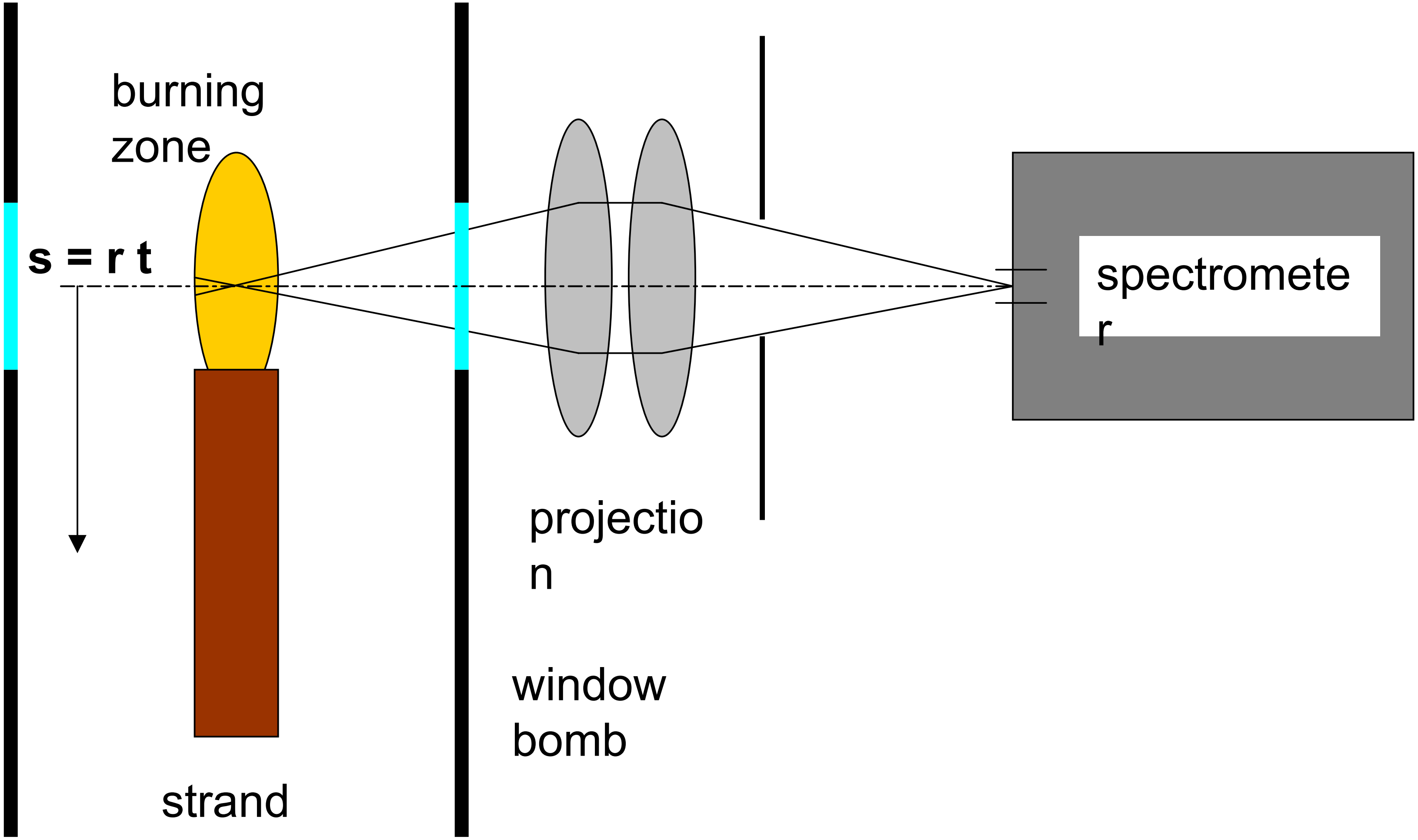
camer
a

digital
picture analysis

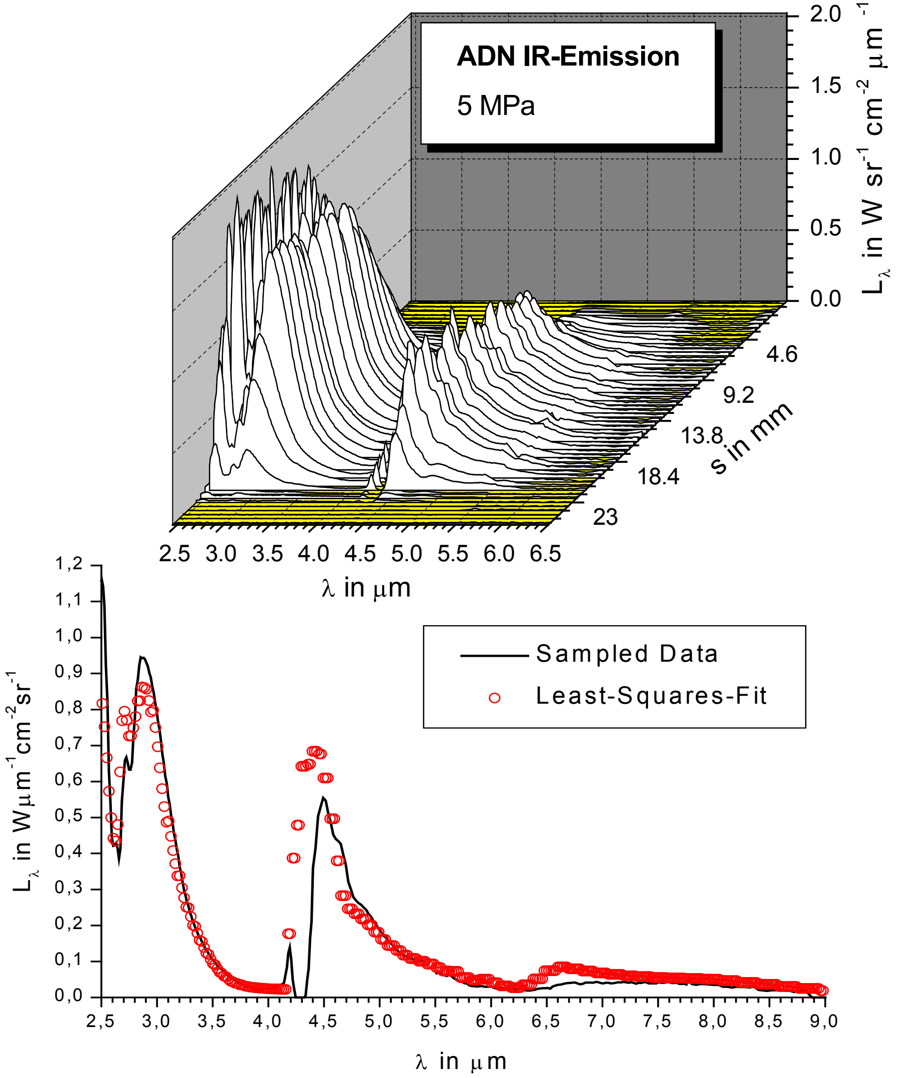
nitrogen
(<13 MPa)

spectromete
r

Strand burner: non-intrusive investigations of burning zone



IR-Spectrum – Fit and Measurement of ADN/Fuel



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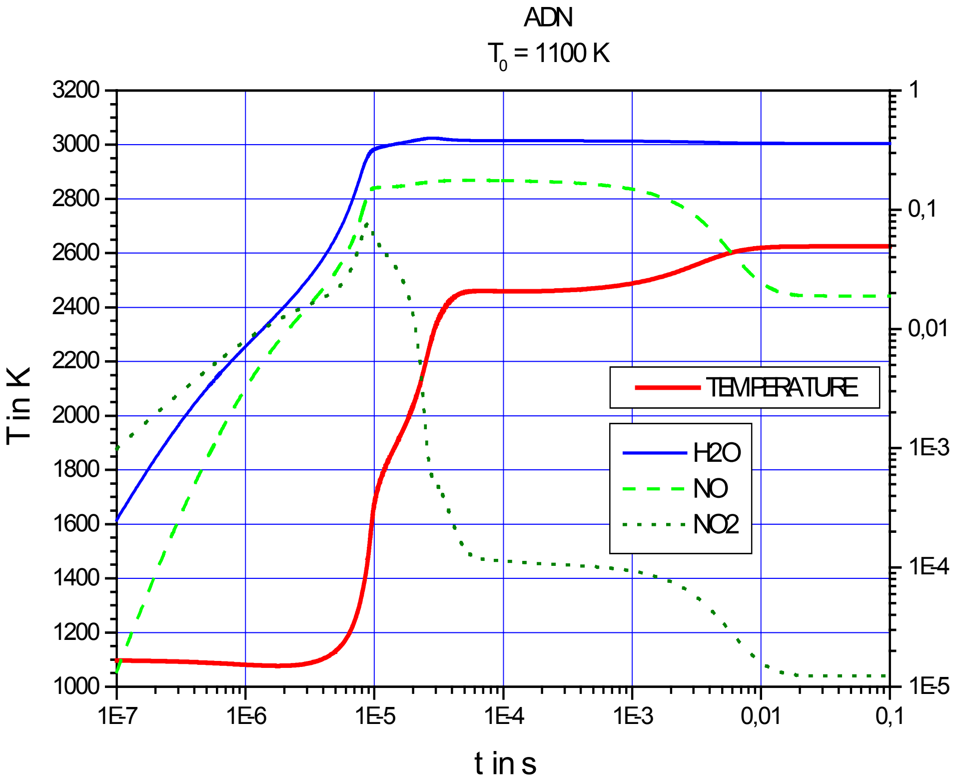
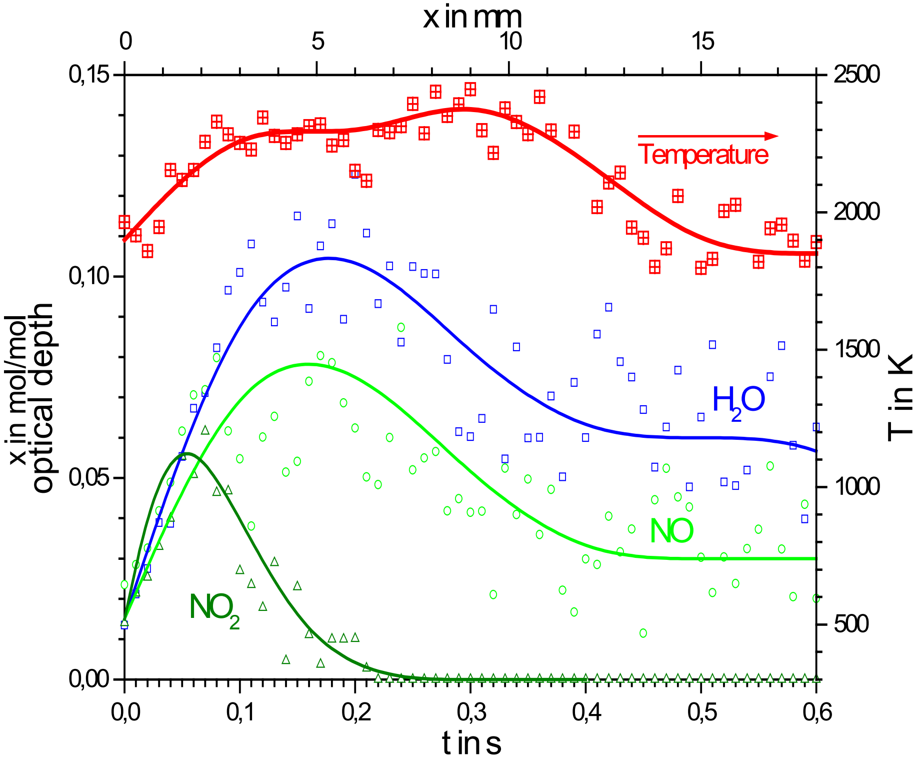
Concentration profiles in the flame zone of ADN

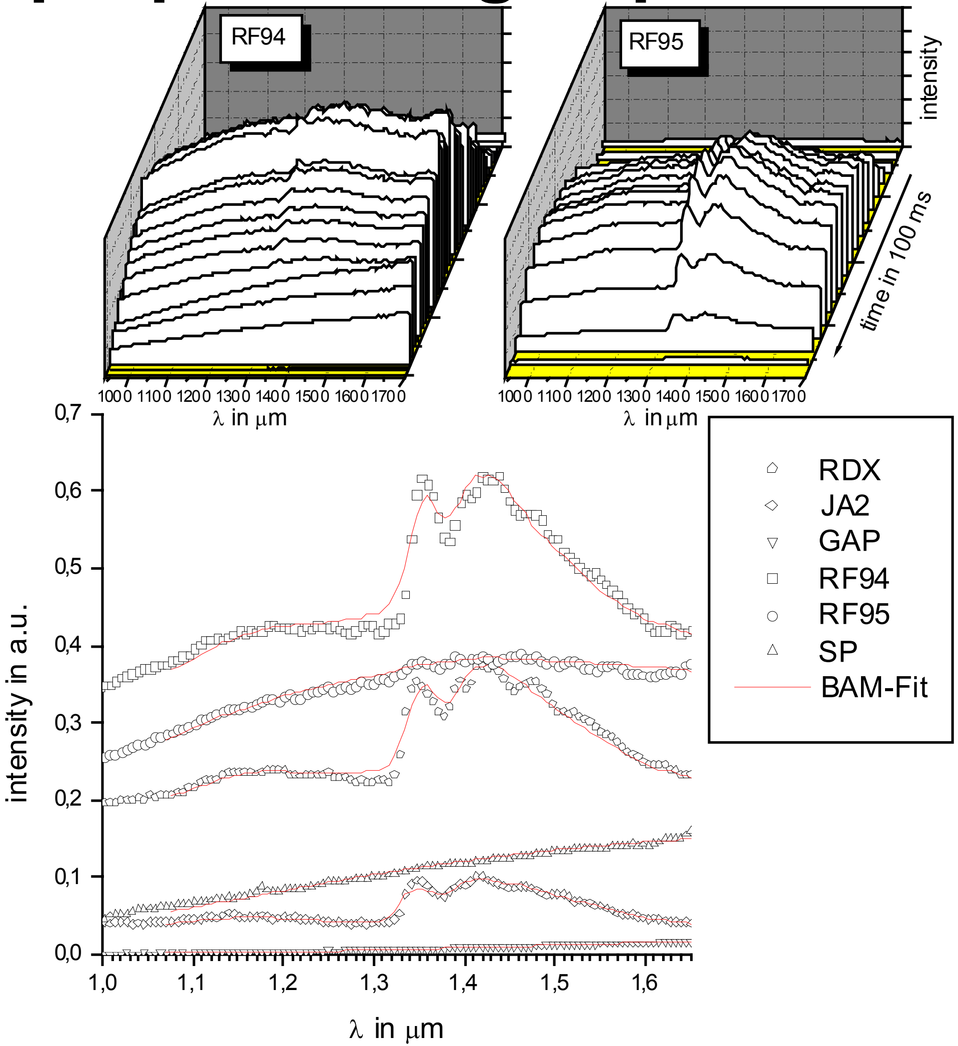


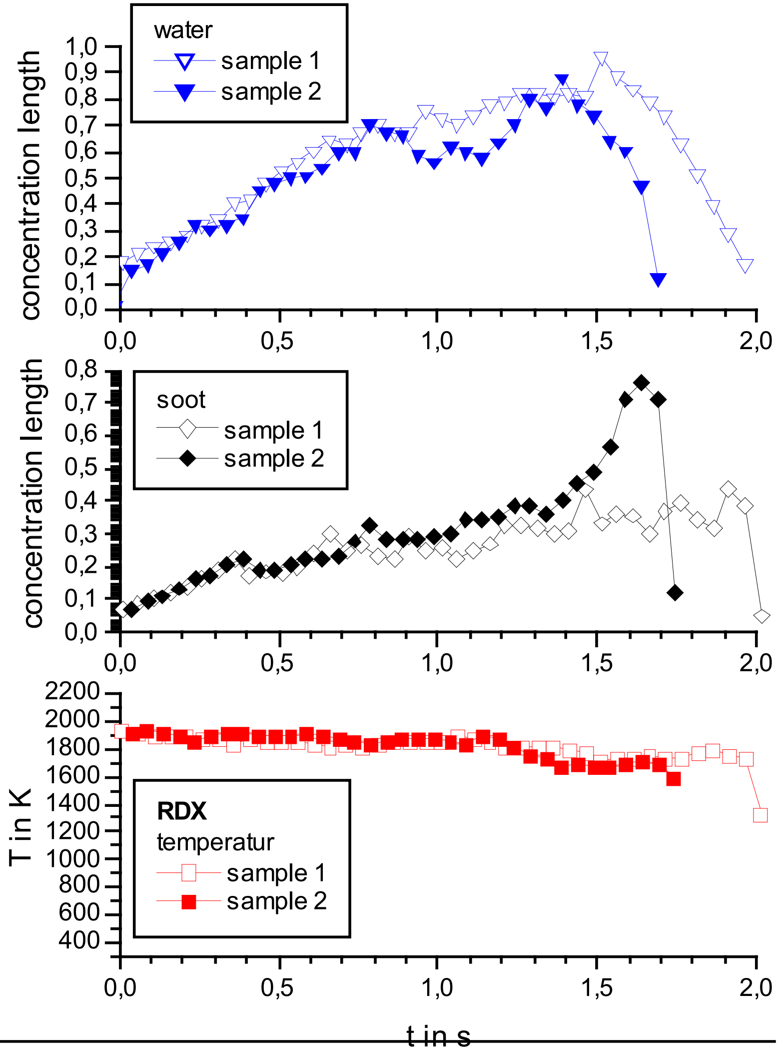
CHEMKIN Simulation



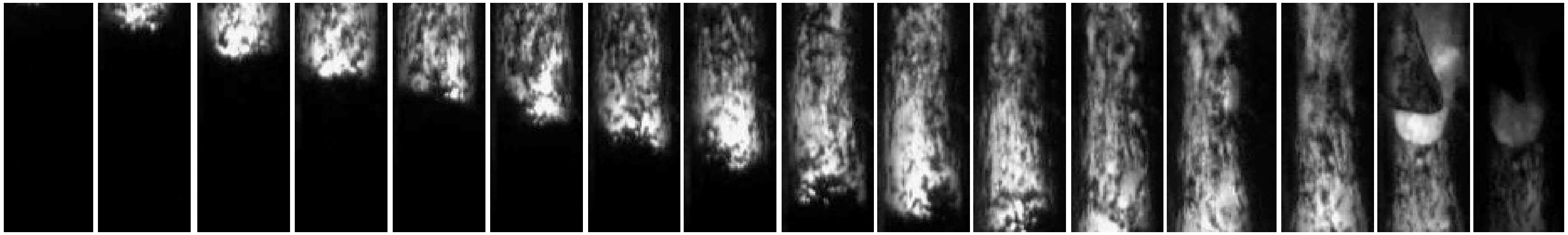
BAM analysis of IR-Spectra

HGS - Flame temperatures determination of propellants, gun powders, gasgenerators

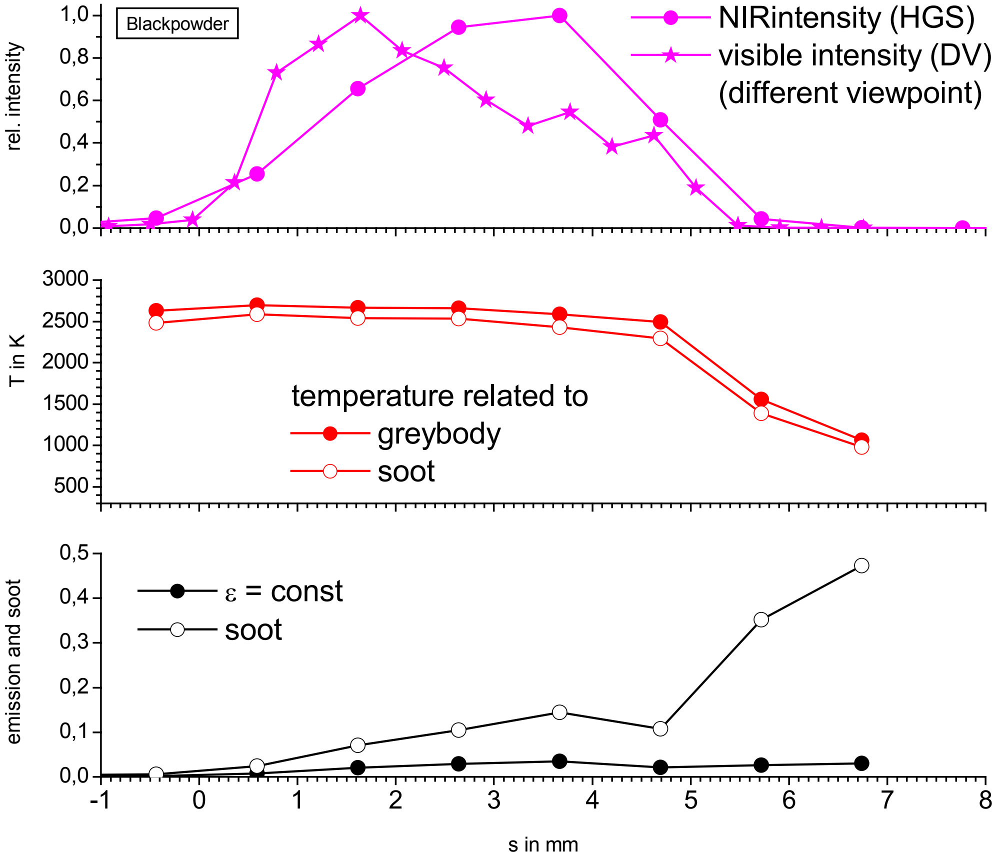




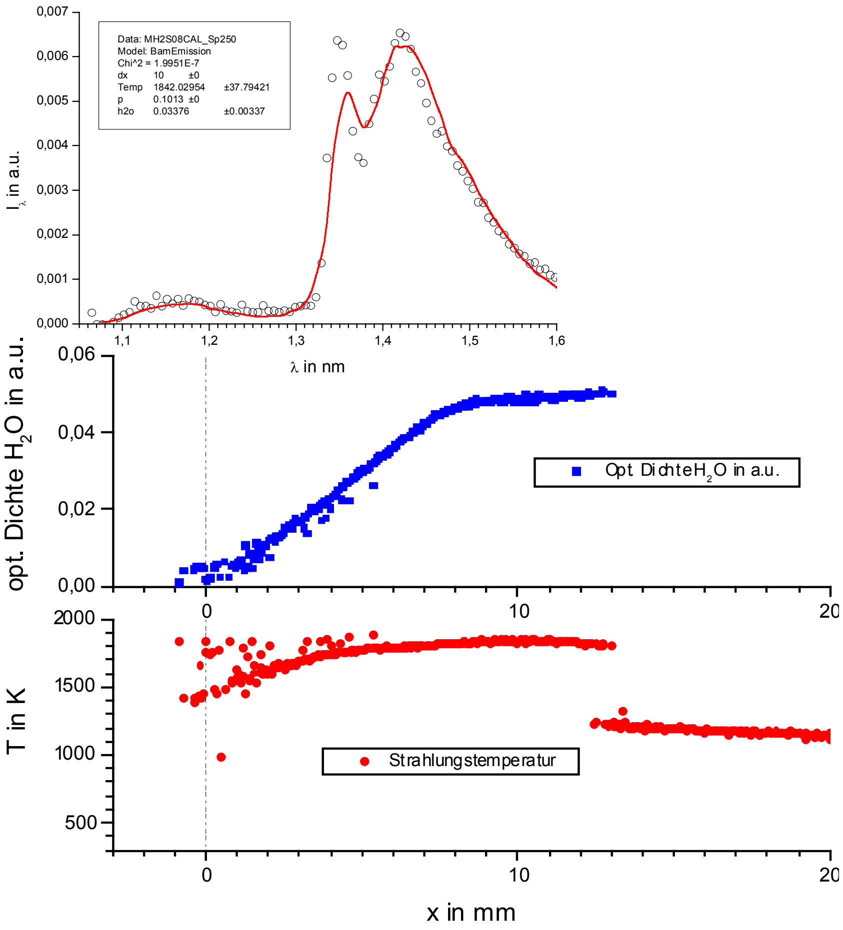
Back powder combustion at 4 MPa

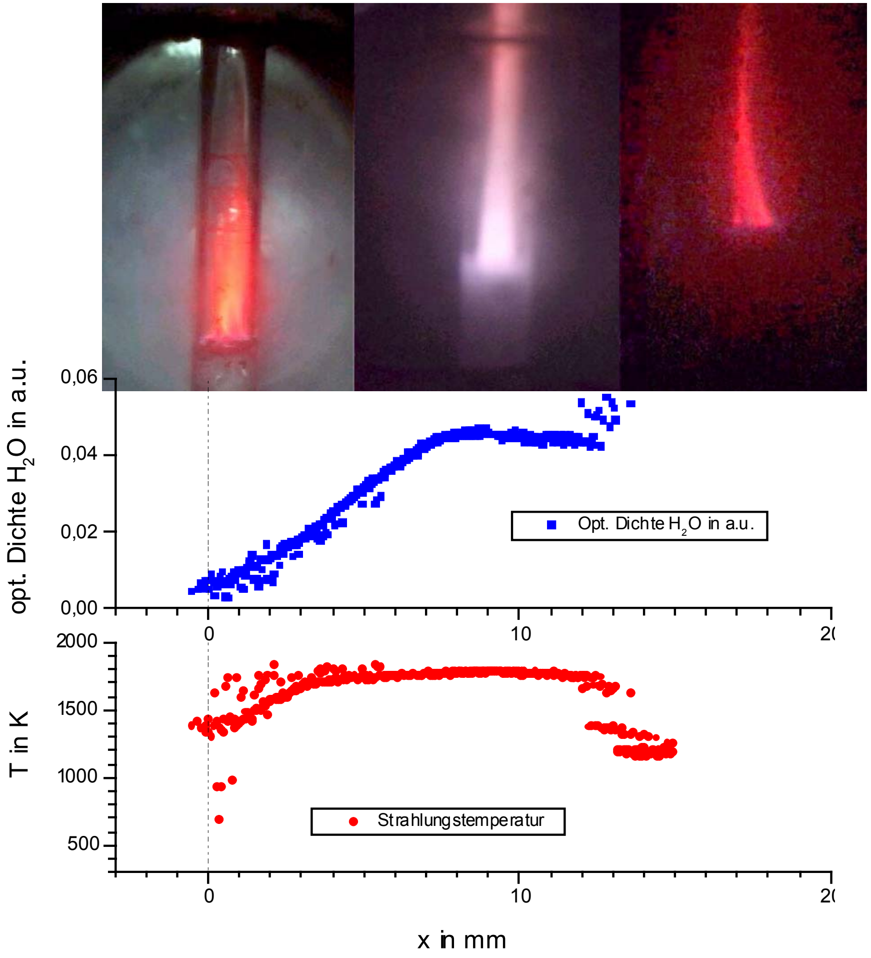


HGS analysis



HGS NIR-Spektrometer: Burning Charakterisation of H_2O_2 (85%)/Methanol Cryogenic Solid Propellants





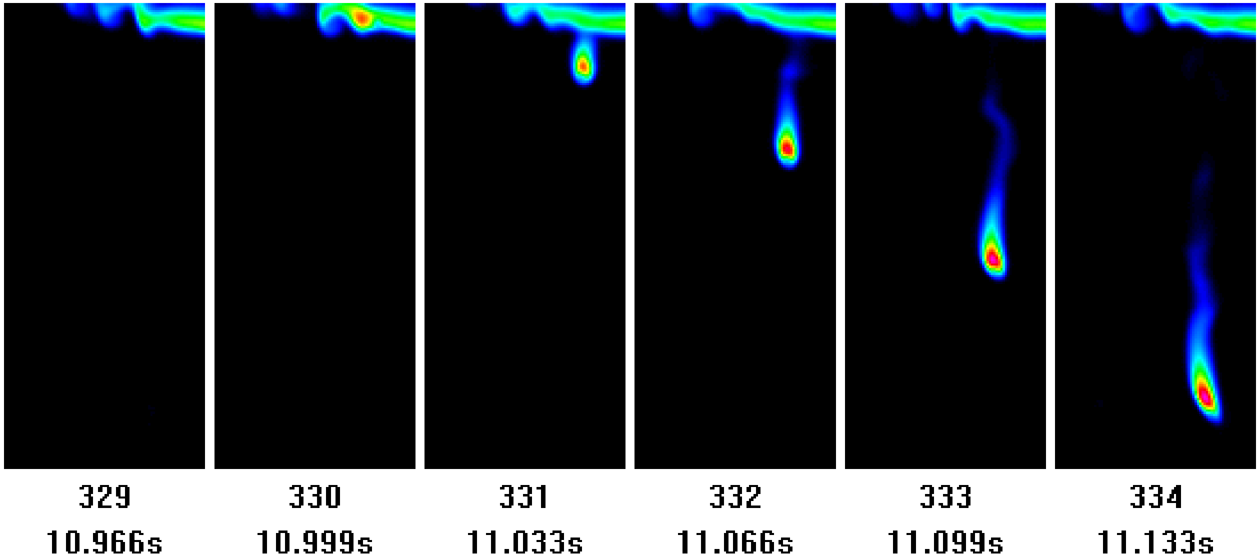
Flüssig (T_0=300 K)

Kryo-Gel (T_0=220 K)

Moving and burning gelled propellant droplets

Highspeed
Video

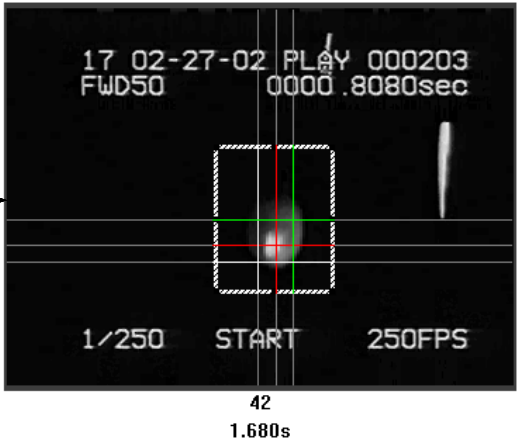
IR-Camera



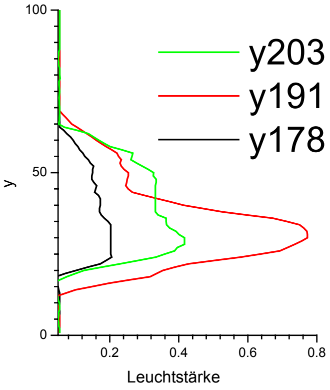
Picture analysis: 2D-distribution of radiation on a single droplet

single picture

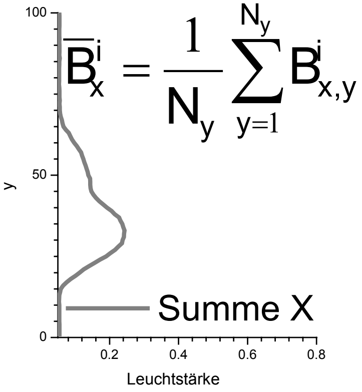
256 intensity steps



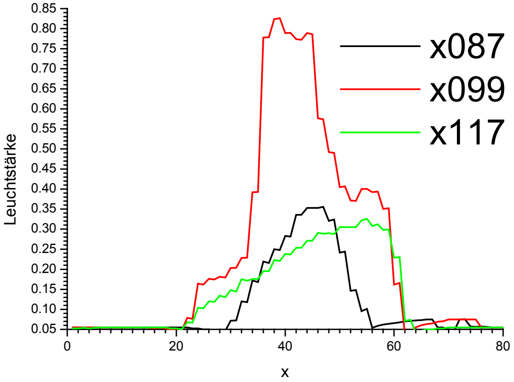
single y-line



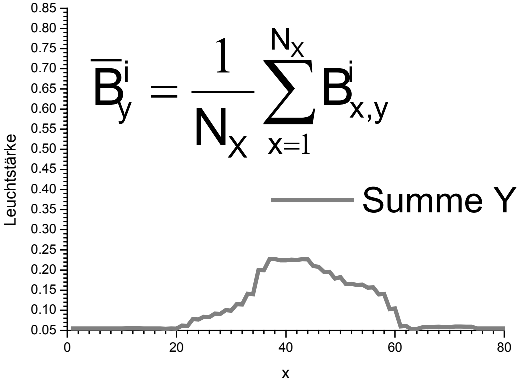
mean value Y



$$\overline{B}_x^i = \frac{1}{N_y}\sum_{y=1}^{N_y} B_{x,y}^i$$

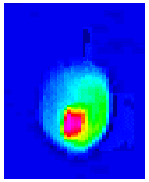


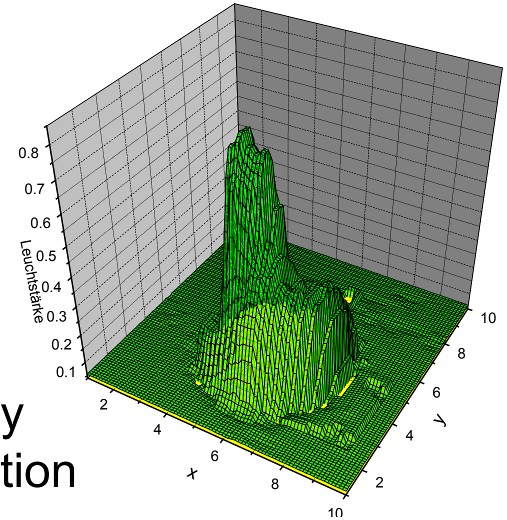
single x-line



$$\overline{B}_y^i = \frac{1}{N_x}\sum_{x=1}^{N_x} B_{x,y}^i$$

Mean value X





Intensity distribution

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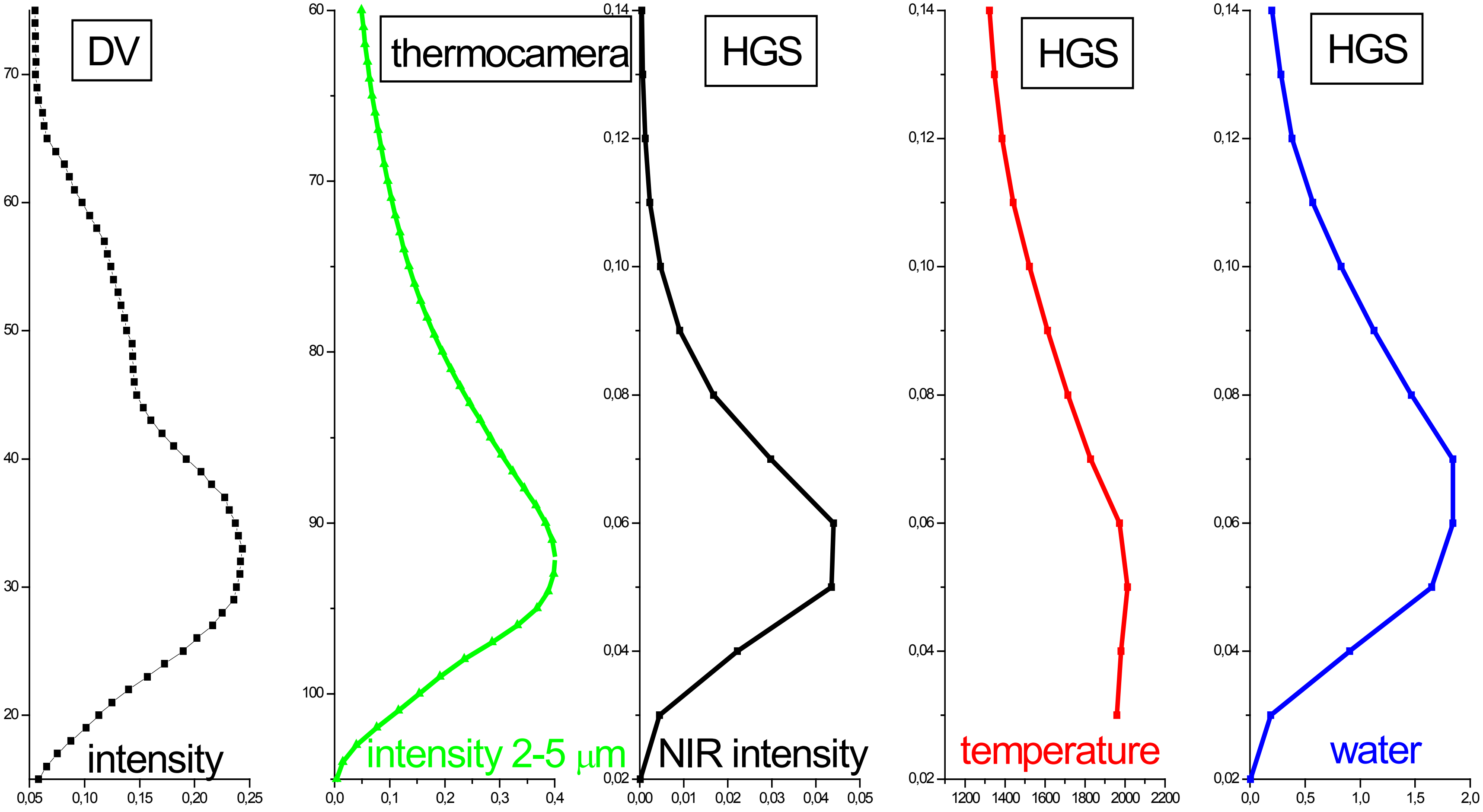
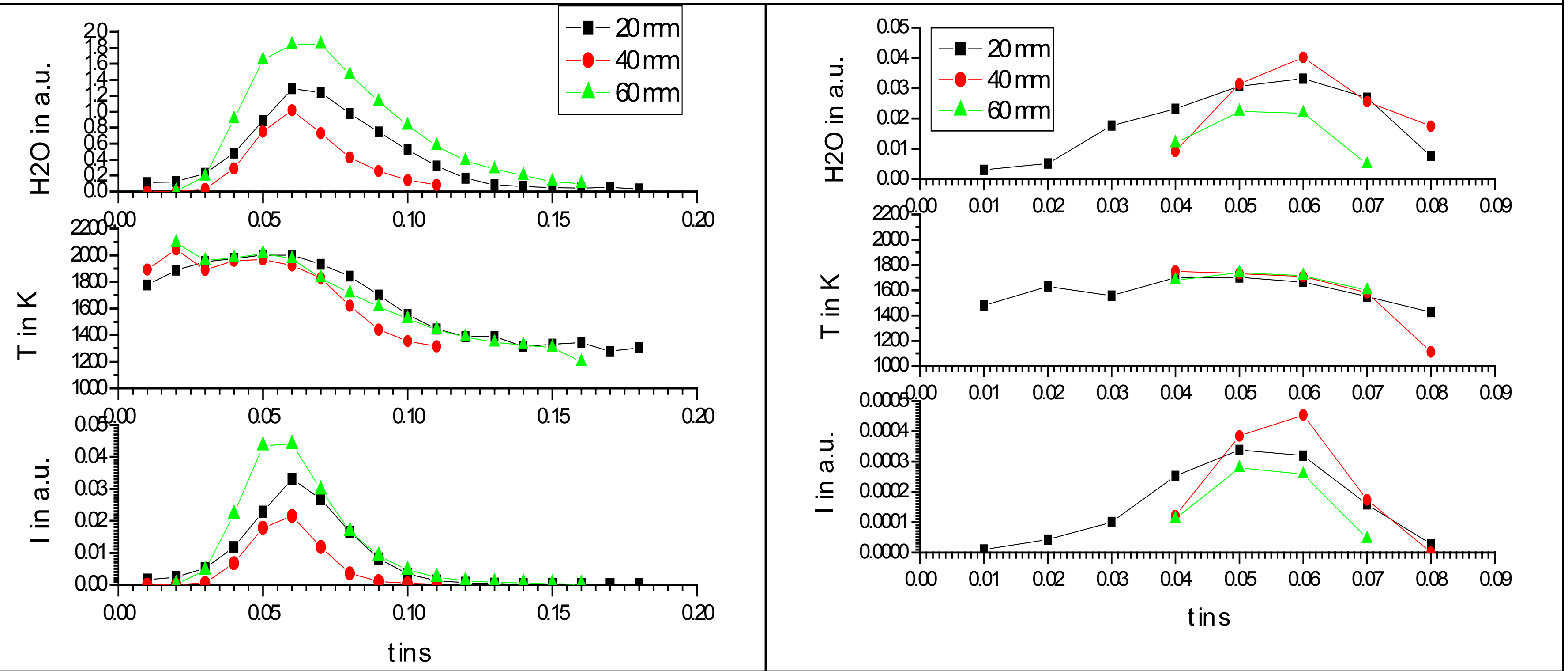
Comparison of DV-, IR-camera and spectral signals



NIR spectra analysis along a moving and burning gelled droplet (concentration length of H_2O, temperature and integrated NIR radiation)

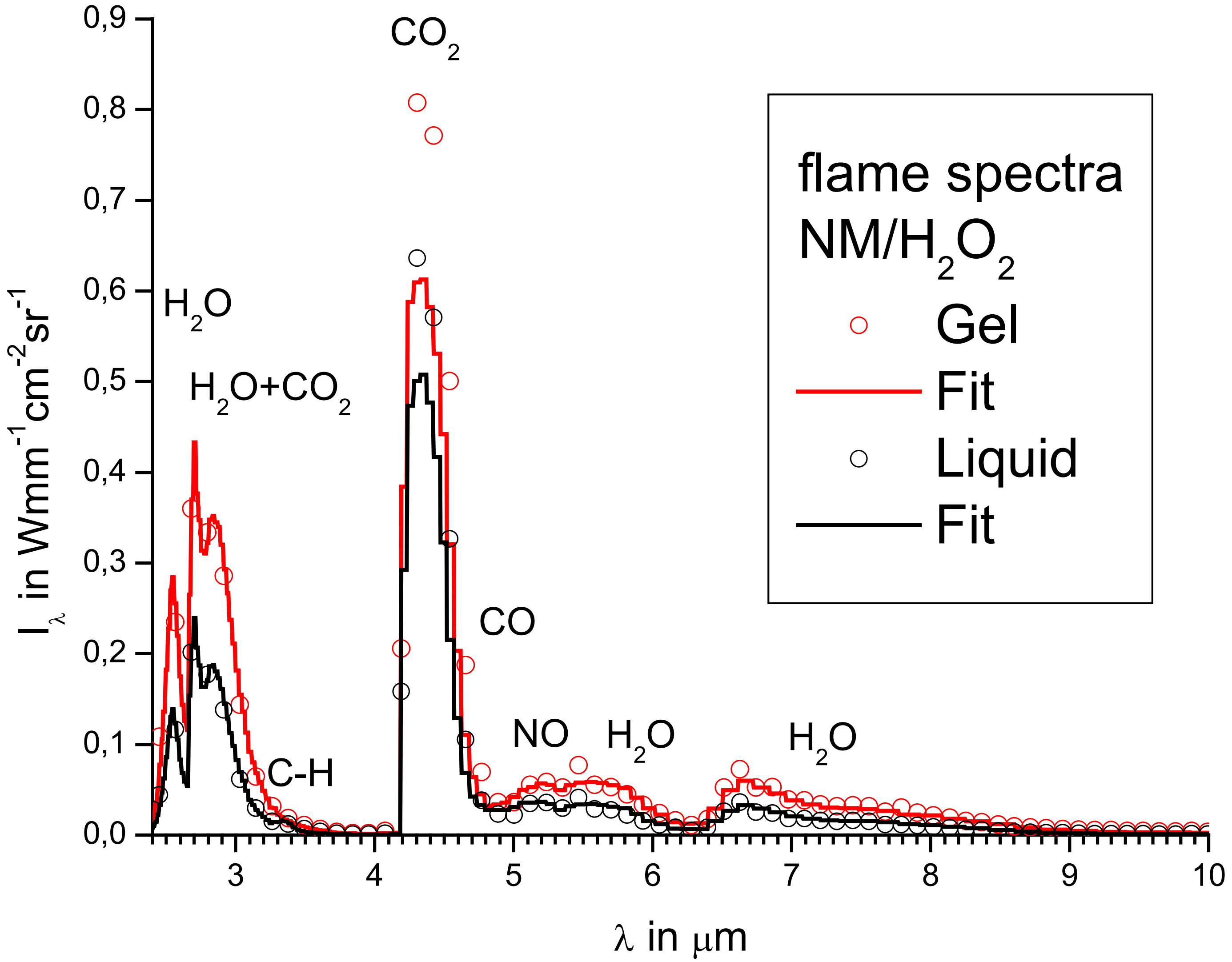
50% nitromethane 50% H_2O_2



gelled propellant (5% aerosil)

liquid propellant

IR-Spectrum of a burning NM/H_2O_2 samples



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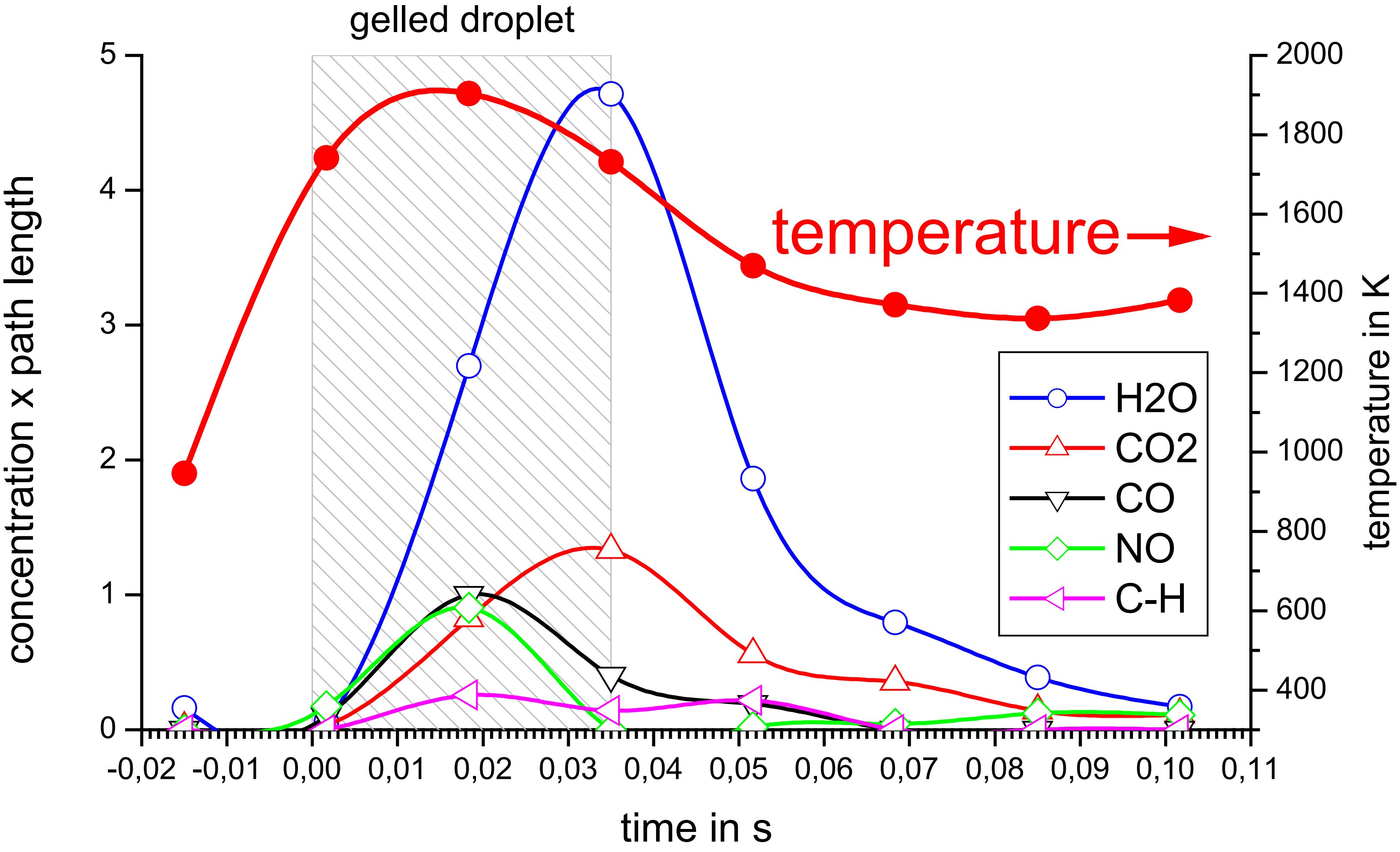
Profile of temperature and species over a moveing and burning droplet



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Time resolved Emissions spectroscopy of Combustion Phenomena

- robust technique under field conditions and long distances
- simple set-ups for non-distrusive measurements (one detector)
- time resolution >100 s^{-1} (1000 s^{-1})
- characterization of flame structure and reaction zones
- simultanious determination of
  - ∗ temperature
  - ∗ main combustion products: CO_2, H_2O, CO, NO, HCl, soot
  - ∗ intermediar products: OH, NH, CH, CN, C_2
  - ∗ metall lines