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SPLINE FUNCTIONS IN EVALUATION OF EXPLOSION LIMIT CURVES FOR GAS MIXTURES

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The paper discusses a new method to approximate the sometimes missing apex point of the explosion limit curves of flammable substances with diluents in air. The base of the new method is to vary the frame points of the co-monotonic splines using *de Casteljau* algorithm. We show several examples for flammable/inert/oxidising gas containing systems – selected by the program TRIANGLE – where the method was applied. Due to the definition of the frame of splines it can be stated that the new method never restricts the explosion range around the apex and shifts the explosion limit curve into the direction of higher inert gas concentrations. This means that the new method can correct the highly "cut down nose" of the co-monotonic splines and gives a safer explosion range of these systems.

Keywords: Ternary flammable systems, inerting, explosion areas, co-monotonic spline curves

Introduction

Inerting of explosive fuel-air mixtures is a frequently applied method in the chemical and related industries to prevent fires and explosions. For this purpose the exact knowledge of the explosion range is required as a function of the flammable, oxidizer and inert gas concentrations.

The CHEMSAFE® database [1], which is world wide available through STN International and Internet, contains rated safety characteristics of flammable liquids, gases, dusts and their mixtures, such as explosion limits, flash points, ignition temperatures, etc. The in-house version of CHEMSAFE® allows a graphical representation of the measured explosion range of ternary systems in triangular diagrams as a function of the concentration of flammable (combustible), oxidising or inert gases.

The TRIANGLE program [6,7,9,10], created by BAM and extended by the common research group of BME and BAM, is used for processing measured values of ternary systems, it provides 2D triangular diagrams for the data processing phase of the explosion area of the gas mixtures. In our latest research we created a new test method to investigate whether the (last) measured connection point between the upper and lower explosion limit curves – the so called apex point – is the real apex point, or it is not the last point of the limiting curves.

Description of the explosion range of ternary systems

Beside the explosion limits and the explosion range other characteristics can be also deduced from triangular or Cartesian explosion diagrams, which parameters explicitly define the dangerous area as they are shown on *Fig 1*.

The IAR (minimum **I**nert gas / **A**ir (oxidising gas) **R**atio) and ICR (minimum **I**nert gas / **C**ombustible **R**atio) lines represent limits in the ternary flammable system: the points lying on the right hand side of IAR line or below the ICR line will not cause an explosion regardless of the added amount of flammable gas.

MAI (**M**inimum required **A**mount of **I**nert gas) and MXC (**M**a**X**imum permissible amount of **C**ombustible) points are intercepts of IAR/ICR lines and the corresponding binary triangle sides. The MOC (**M**aximum **O**xidising gas **C**ontent) is given by the

tangent line of the explosion limit curve parallel with the flammable-inert side of the triangle. In some cases this line passes through the apex point .

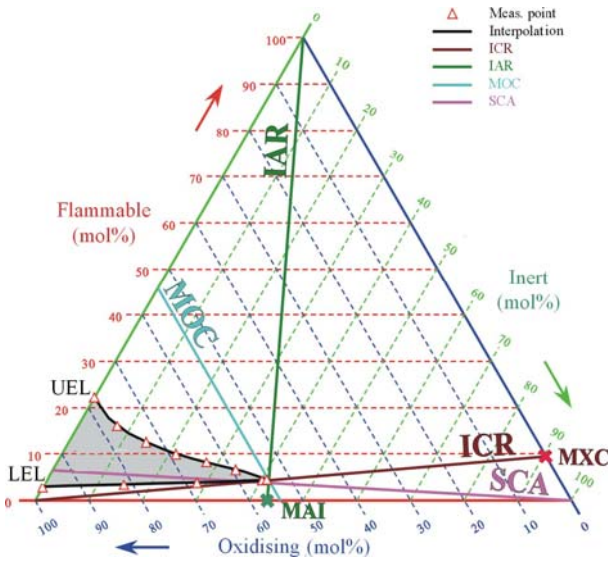

Fig. 1: Characteristics of the explosion area

The LEL (**L**ower **E**xplosion **L**imit) and UEL (**U**pper **E**xplosion **L**imit) curves are generated around the explosion area by applying numerical interpolation on the measured data. Having evaluated the characteristic values of the system the TRIANGLE program returns the results in tables and in ternary diagrams both in Cartesian and in triangle co-ordinates.

Most of the above mentioned characteristics are deduced from the common point of the LEL and UEL curves, from the so called apex point, and for the ICR line and the MXC point we use a tangent line of the LEL curve. These calculations require the best possible numerical approximation of the explosion limit curves and of their apex point.

Application of co-monotonic vector splines

Co-monotonic parametric vector splines possess the best numerical properties for the approximation of ternary explosion limit curves [2,3,4,5,8]. The earlier used Akima splines failed to describe several systems, where the LEL or the UEL curve was not monotonic or the concatenation of the two explosion curves couldn't be considered as an only function of the flammable gas concentration.

As a result of our previous research [6,9], we created subroutines for the co-monotonic parametric vector splines and built them in the TRIANGLE program. Testing this extension of the software we have found several ternary data sets, which didn't contain enough measurements around the most critical apex of their explosion curves. To select these data sets, we made the program to give an alert in these cases, and to offer the user the possibilities of sketching an "open apex" curve, typing in an apex from another source, or trying to make up the apex based on the last two points of the LEL and of the UEL curves.

The make up of the apex, based on the last two points of the LEL and of the UEL curves gives also a possibility to investigate other - "full" - data sets whether the "common" point of the LEL and UEL can be considered as a real apex point, or it rather belongs only to the LEL or only to the UEL curve.

The theoretical background of the apex-make-up is the de Casteljau algorithm. This algorithm offers a numerically very simple way to evaluate an n-dimensional point of a parametric (cubic) co-monotonic spline curve. The algorithm and the resulted point are shown on *Fig.2.*

$$\underline{p}_0^1(t) = (1-t)\cdot \underline{p}_0 + t\cdot \underline{p}_1 \qquad \underline{p}_0^2(t) = (1-t)\cdot \underline{p}_0^1 + t\cdot \underline{p}_1^1 \qquad \underline{p}_0^3(t) = (1-t)\cdot \underline{p}_0^2 + t\cdot \underline{p}_1^2$$
$$\underline{p}_1^1(t) = (1-t)\cdot \underline{p}_1 + t\cdot \underline{p}_2 \qquad \underline{p}_1^2(t) = (1-t)\cdot \underline{p}_1^1 + t\cdot \underline{p}_2^1 \qquad t \in [0;1]$$
$$\underline{p}_2^1(t) = (1-t)\cdot \underline{p}_2 + t\cdot \underline{p}_3$$

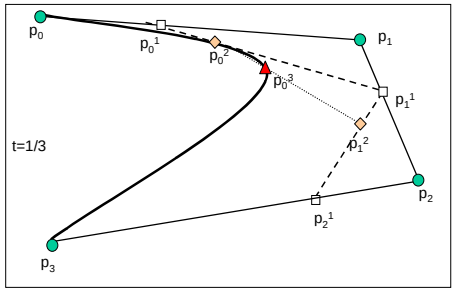

Fig. 2.: The four frame points of a co-monotonic spline and evaluating p_0^3 at t=1/3

To determine the p_0, p_1, p_2 and p_3 frame points of the co-monotonic spline we have used the last two points of the UEL curve, and the last two points of the LEL curve. If the measured data set contained an (assumed) apex point, in the first step of our algorithm we truncated the data set by this assumed apex. We evaluated a co-monotonic spline based on the remained last four points.

In *Tables 1 and 2* we show the steps of the frame point calculations for the systems NH_3+N_2+Air and CH_4+CO_2+Air, in this second case we give a description of the steps in every detail. One can see the frame points (black squares), and the result of the apex test for the NH_3+N_2+Air system on *Fig 3*, and for the CH_4+CO_2+Air system on *Fig. 4.*

NH3+N2+Air T=24C P=1,03 bar

For the secant-intercept:

	N2	NH3
LEL	14	15,8
	16	16,15
UEL	16	16,9
	14	18,05

de Casteljau frame t*= 0,66

	xo	yo	slope		x	y
secant1	16	16,15	0,175	p0	16	16,2
secant2	16	16,9	-0,58	p1	16,7	16,3
intercept	17	16,325		p2	16,7	16,5
delta(x)	1,00			p3	16	16,9
	1,00					
ratio(2/1)	1,00	slope ratio	3,3			

Table 1: Frame point calculation (symmetric case)

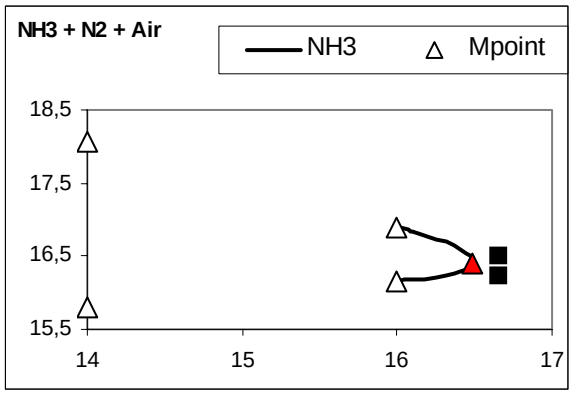

Fig. 3: Apex test (result: the real apex was measured)

In the case of NH_3+N_2+Air system the skipped apex lies on the approximating spline as a real apex – this means that the measured apex is a real one.

The apex test suggests for the CH_4+CO_2+Air system that the assumed apex is not a real one. The measured point lies on the UEL curve, and a new apex point is offered showing 1% relative difference in the inert gas concentration. In this case the steps of the frame point calculations show asymmetry because the inert gas differences of the last two points on the LEL and UEL curves are not equal. The slope ratio is also in this system not too big, what means that the asymmetry is only in the different distances of the measured points.

CH4+CO2+Air T=24C P=1 bar

For the secant-intercept:

	CO2	CH4
LEL	25	5,7
	28,5	**6**
UEL	**27,8**	**7**
	25	7,9

de Casteljau frame t*= 0,75

	xo	yo	slope		x	y
secant1	28,5	6	**0,086**	p0	28,5	6
secant2	27,8	7	**-0,32**	p1	29,5	6,1
intercept	**30,40**	**6,16**		p2	29,8	6,4
delta(x)1,90				p3	27,8	7
2,60						
			slope			
ratio(2/1)1,37			**ratio3,75**			

Table 2: Frame point calculation (asymmetric case)

To see clearly the meaning of the results now we show step by step the frame point algorithm and the apex calculation of the asymmetric case.

The bold points of *Table 2* on LEL / UEL (28,5 ; 6) and (27,8 ; 7) are chosen for the frame points p_0 and p_3. Using the other two points – (25 ; 5,7) on LEL and (25 ; 7,9) on UEL – we determined the equation of the lines passing through the given points of LEL/UEL. The intercept (p_m) and the slopes (s1 and s2) of the two lines and the ratio of the two slopes contain the shaded cells of *Table 2.*

The next step is to calculate the t^* parameter that determines the p_2 frame point on the line segment of p_3 and p_m:

If abs(s2/s1)<5 **then** t^*=abs(s2/s1)/5 **else** t^*=0,99

with this t^* : $p_2 = p_3 + t^* \cdot (p_m - p_3)$ *(1/a)*

Now we calculate the ratio of the horizontal distances between the secant line intercept and p_0 / p_3 LEL / UEL points: *ratio(2/1)=2,6/1,9=1,37=a21*

with this a21 : $p_1 = p_0 + t^* \cdot (p_m - p_0)/a21$ *(1/b)*

Having determined the missing two frame points, any arbitrary point of the interpolating co-monotonic spline can be calculated by the de Casteljau algorithm.

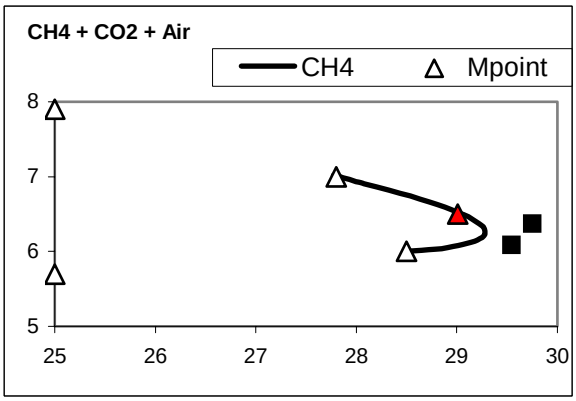

Fig. 4: Apex test (result: not the real apex was measured)

The apex calculation is very simple: we have to determine the maximal abscissa of the co-monotonic spline.

The key of this apex calculation lies in the parameter t^* that determines by the missing two frame points the apex, too. The original formula for t^* is the following:

If abs(s2/s1)<c **then** t^*=abs(s2/s1)/c **else** t^*=1-k *(2)*

The values of parameters c and k can be determined by minimising the function given in *Eq. 3*

$$F(c,k) = \sum_{j=1}^{sysnum} distance\left(apex_{meas} - spline(c,k)\right) \qquad (3)$$

Naturally, we have the better c and k parameters the more complete system we involve into the minimisation. In Eq. 1/a we used c and k determined by the systems shown in *Table 3* (Group 1/a).

The above investigated NH_3+N_2+Air and CH_4+CO_2+Air systems consist of enough measured points at the apex area, because the interpolating spline based on the truncated system passes through the skipped "apex". The next two systems shown on *Figs 5 and 6* don't have this property.

The Ethene + CO_2 + Air system was measured at T=20 C temperature and P=100 bar pressure. The truncated data set doesn't contain enough information to evaluate the frame points for an interpolating function passing through the skipped apex.

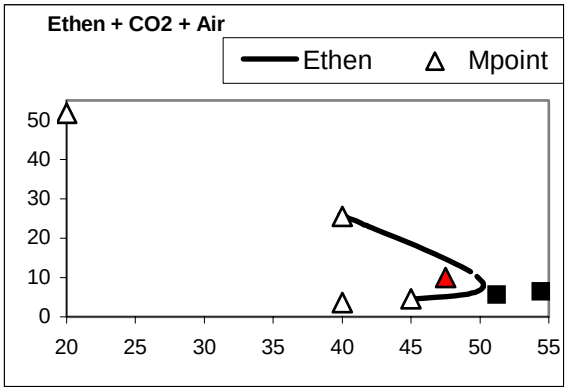

Fig. 5: Apex test (after truncation the skipped apex is in the explosion area)

Quite the same thing occurs in the case of Propane + $C_2H_2F_4$ + Air system, measured at T=20 C and P=1 bar. The only difference is between the two last systems, that in the first system the acceptance of the new apex is uneconomic, while in the second one it is dangerous.

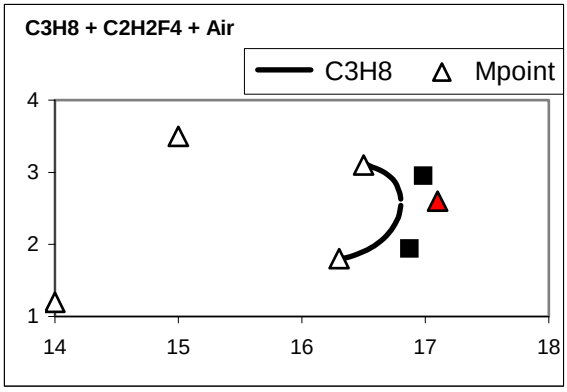

Fig. 6: Apex test (after truncation the skipped apex is out of the explosion area)

In both last cases we have got the information that the truncation is not allowed. So we have to repeat the procedure, but now without truncation.

Application of the new apex test for different systems

The two-step apex test we have applied for 45 different ternary systems selected by the TRIANGLE program. First we investigated 23 systems where in the most cases we considered the systems as at the apex area fully measured ones. We summarize the test results in *Tables 3, 4, 5 and 6.*

The group 1/a contains 8 systems where after truncation the spline passes through the original apex point. However, the apex test results only for the first system that the measured apex was a real one. For the other 7 system a safer apex (bigger inert and smaller flammable gas concentration) is offered.

	System	T[C]	p[bar]
1	NH3+N2+Air	24	1,03
2	CH4+CO2+Air	24	1
3	C2H6+CO2+Air	24	1
4	CO+(CO2+H2O)+Air	110	1
5	CO+(N2+H2O)+Air	400	1
6	CH4+Ar+Air	340	1
7	(99%CO+1%H2)+N2+Air	20	1
8	Isobutene+N2+Air	200	1

Table 3: Systems of 1/a group

	Measured apex			Apex calculations		
	Inert (%)	Flamm (%)	trunc.	In(%) new	Fl(%) new	Rel diff%
1	16,5	16,4	pass	old		
2	29	6,5	pass	**29,3**	**6,3**	**1,0**
3	39,7	4	pass	**41,1**	**3,6**	**3,5**
4	53,88	17,05	pass	**53,92**	**16,34**	**0,07**
5	83,62	5,27	pass	**84,9**	**5,94**	**1,5**
6	70,86	2,15	pass	**73,1**	**2,32**	**3,2**
7	64	11,5	pass	**66**	**12,4**	**3,1**
8	55	1,6	pass	**57,3**	**1,7**	**4,2**

Table 4: Apex results of 1/a group

The group 1/b consists of 15 systems where after truncation the spline doesn't pass through the original apex point. After the first step of the apex step in the group 1/b the second step (without truncation) is carried out, too. The result of the second step is that for 10 systems the data set contains the real apex, and only in the remained 5 cases is a safer apex offered.

	System	T[C]	p[bar]
1	Acetone+N2+O2	20	1
2	C3H8+C2H2F4+Air	20	1
3	C3H8+N2+Air	20	1
4	Ethene+N2+Air	20	1
5	Ethene+N2+Air	20	100
6	Ethene+CO2+Air	20	1
7	Ethene+CO2+Air	20	100
8	Ethene+N2+Air	100	100
9	PO+CO2+Air	20	1
10	CO+(CO2+H2O)+Air	70	1
11	CO+(CO2+H2O)+Air	200	1
12	CO+(Ar+H2O)+Air	100	1
13	2Me-1Propene+CO2+Air	20	1
14	IsoButen+H2O+Air	100	1
15	2Me-1Propene+H2O+Air	200	1

Table 5: Systems of 1/b group

	Measured apex			Apex calculations		
	Inert (%)	Flamm (%)	trunc.	In(%) new	Fl(%) new	Rel diff%
1	82,92	3,11	in	old		
2	17,1	2,6	out	old		
3	53	2,4	in	old		
4	55,5	3,4	out	old		
5	58	10	in	old		
6	41,5	4,7	out	old		
7	47,5	10	in	old		
8	62	12,3	in	old		
9	47,2	3,7	in	old		
10	52,78	17,04	out	old		
11	59,23	16,61	out	**59,56**	**15,52**	**0,6**
12	75,5	10,14	in	**77,2**	**8**	**2,3**
13	32,9	2,5	out	**33,6**	**2,6**	**2,1**
14	32,3	2	in	**33,2**	**2,4**	**2,8**
15	36,2	1,9	in	**37,4**	**2,3**	**3,3**

Table 6: Apex results of 1/b group

	System	T[C]	p[bar]
1	Ethane+N2+Air	20	1
2	2Me-Propane+H2O+Air	100	1

Table 7: Systems of 2/a group

	Measured apex			Apex calculations		
	Inert (%)	Flamm (%)	trunc.	In(%) new	Fl(%) new	Rel diff%
1	53,9	2,9	pass	**54,5**	**2,7**	**1,0**
2	35,6	2,0	pass	**36,4**	**2,2**	**2,2**

Table 8: Apex results of 2/a group

	System	T[C]	p[bar]
1	1-Butene+N2+Air	24	1
2	Methane+H2O+Air	100	1
3	Methane+CO2+Air	300	1
4	Methane+CO2+Air	340	1
5	Methane+CO2+Air	400	1
6	Methane+H2O+O2	200	1
7	Ethane+CO2+Air	20	1
8	Propane+CO2+Air	20	1
9	Propane+CO2+Air	100	1
10	Propane+CO2+Air	250	1
11	Propane+CO2+Air	400	1
12	Propane+H2O+Air	200	1
13	Isobutane+N2+Air	20	1
14	Isobutane+N2+Air	100	1
15	2Me-Propane+CO2+Air	100	1
16	Isobutane+H2O+Air	250	1
17	Propene+N2+Air	100	1
18	Propene+N2+Air	250	1
19	Propene+CO2+Air	20	1
20	Propene+CO2+Air	100	1

Table 7: Systems of 2/b group

	Measured apex			Apex calculations		
	Inert (%)	Flamm (%)	trunc.	In(%) new	Fl(%) new	Rel diff%
1	51,0	1,8	pass(bRd)	**51,3**	**2,0**	**0,6**
2	34,2	6,5	out	**34,8**	**6,2**	**1,8**
3	38,5	5,6	in	old		
4	40,5	5,3	in	**40,6**	**5,4**	**0,2**
5	43,7	4,9	out	old		
6	76,3	9,0	out	old		
7	38,1	3,4	pass(bRd)	**40,4**	**3,6**	**6,0**
8	37,1	2,8	in	**37,7**	**3,0**	**1,7**
9	34,0	2,4	pass(bRd)	**40,9**	**2,9**	**20,2**
10	42,1	2,1	out	**47,1**	**2,3**	**11,8**
11	54,0	1,7	out	**56,0**	**1,9**	**3,7**
12	42,0	2,8	out	**42,5**	**2,6**	**1,3**
13	47,9	2,6	out	**50,4**	**2,2**	**5,3**
14	53,0	1,8	in	**53,8**	**2,1**	**1,6**
15	36,1	3,2	out	**36,9**	**2,8**	**2,1**
16	39,0	1,6	in	**39,7**	**1,8**	**1,7**
17	55,1	1,9	out	**60,5**	**2,0**	**9,9**
18	50,0	4,0	out	**61,8**	**1,9**	**23,6**
19	35,0	2,8	out	**39,1**	**3,0**	**11,6**
20	40,1	2,8	in	**42,1**	**3,1**	**4,9**

Table 10: Apex results of 2/b group

The second group of systems investigated consists of 22 ternary systems selected by the TRIANGLE program. Among these systems there were several ones on higher temperature measured systems and some ones where the TRIANGLE gave the “open apex” alert. As we see in *Tables 9 and 10*, for 20 systems the two-step apex test was necessary.

In the case of three systems (group 2/b, systems 1, 7 and 9) even the approximating spline evaluated from the truncated system passed through the skipped measured “apex”, the measured apex was not a real one, and the apex-make-up offered such a different new apex (relative difference in inert gas concentration was bigger than 5%), that its acceptance would be too expensive. Also in these cases we continued the apex test by its second step. It gave a quite good result for the first system, but for the seventh and ninth the big difference remained. In these cases, as well as for the 10, 13, 17, 18, 19 systems additional measurements are suggested.

On the *Fig. 7* we show the 1-Propene + N_2 + Air system (18), measured at T=250 C, P=1 bar. Considering, that in the measured data set the smallest flammable concentration on the LEL curve is 0,9 mol%, and the biggest on the UEL curve is 13,6 mol%, none of the last two measured points on the LEL or UEL (1,3 mol% and 4 mol%) can be assumed as a real apex point.

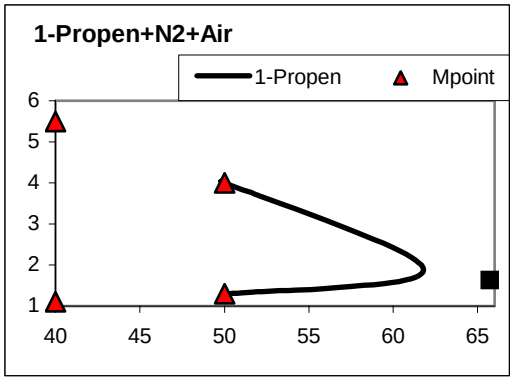

Fig. 7: 2/b group, 18. system: open apex in the measured data

Conclusions

For correct description of explosion areas for ternary gas mixtures containing flammable gas, we created a new test method to investigate whether the (last) measured connection point between the upper and lower explosion limit curves – the so called apex point – can be accepted as the real apex point, or it is safer to reject this hypothesis and try to measure more point around the apex. We tested by the new method several flammable/inert/oxidising gas containing systems – selected by the program TRIANGLE. As result we can state, that using all the information hidden in the measured data, by the new method we can either correct the highly "cut down nose" of the co-monotonic splines or recognize that more measured data are necessary. The application of our new method gives a safer explosion range for the investigated systems.

The here presented algorithm also shows promising results for using as a tool for planning experiments. According to the new EC standard prEN 14756, "Determination of the limiting oxygen concentration (LOC) for gases and vapours", which is now under approval, offers two experimental methods for determination of LOC, the so called "short procedure" - for substances with small explosion range - and the "extended procedure" for substances with a large explosion range. In this last case a spline approximation is needed for the determination of the apex of the explosion curve and the LOC value from the upper explosion limits. The Akima Spline overestimates many times the apex area, which is very uneconomic. Also in these cases an application of the new method would be very desirable.

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List of Symbols

a21	Inert concentration differences' ratio
bRd	Big Relative Difference in meas./calc. apex
c and k	Parameters for apex calculation
IAR	Minimum Inert gas / Air (Oxidising gas) ratio
ICR	Minimum Inert gas / Combustible Ratio
LEL	Lower Explosion Limit
MAI	Minimum required Amount of Inert gas
MOC	Maximum Oxidising gas Content
MXC	MaXimum permissible Amount of Combustible gas
P	Pressure, bar
p_0,p_1,p_2,p_3	Spline frame points
p_m	Secant lines' intercept
s1, s2	Slopes
T	Temperature, K or C
t^*	Frame points' parameter
UEL	Upper Explosion Limit
(x,y)	Cartesian co-ordinates

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