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UNCERTAINTY OF QUALITATIVE RESULTS OF CHEMICAL ANALYSES IN FIRE SAFETY

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ABSTRACT

The article deals with the current issue of evaluation of qualitative results uncertainty of chemical analyses in the example of chromatographic analyses of specimens of accelerants from a fire place with the SPME-GC/MS technique. The suitability of this technique demonstrates with the results of alidation measurements of analytical characteristics: sensitivity, detection limits, linearity, selectivity and repeatability. It characterizes briefly the current state of knowledge in the area and applies the Bayesian theory for the unconditional "a-priori" probability of an analyte presence in a sample, P (H) of 0.5 and 0.95 for calculation estimates the "a-posteriori" conditional probability of the presence of the analyte in the sample relative to the experimental evidence, P (H / E) with the results of 0.97 and 0.98. This result can be interpreted as a high level of assurance of the hypothesis of presence of the analyte in the sample. In conclusion it is stated that the knowledge can also be applied in the field of construction not only in qualitative analyses of building materials / products, e. g, by FTIR, but also in the probability risk assessment.

KEYWORDS

Qualitative chemical analyses, GC/MS, Fire debris, Samples, Accelerants, Uncertainty estimation Bayes´ theorem, Fire technical expertise, Fire safety of buildings.

INTRODUCTION

ČSN EN ISO/IEC 17025 [1] demands accredited testing laboratories to have and use procedures for the assessment of the measurements of uncertainties. During their estimation, they must consider all the components of the uncertainties while using proper methods of the analyses. The introduction of a conception of the test data results according to mentioned standard is specified, among others, by the document ILAC No. G 17:2002 [2]. It is claimed that it relates to the quantitative measurement/test results according to the definition of the uncertainty. The definitions and procedures of the estimation of uncertainties are stated by e.g. the GUM [4] and a series of other documents, [5]-[8]. The estimation procedure can be characterized by setting the components of uncertainties: by the procedure A including the random statistical mistakes, by the procedure B expressing components of uncertainties from their known sources. Consequently, the combined standard uncertainty of measurement is calculated according to the law of spreading uncertainties from its particular components and the so-called extended uncertainty, usually with the coverage factor, k = 2 estimating the interval around a measured result of such a size that the correct result lies in it with the 95 % certainty.

The purpose of qualitative fire test determinations, e.g. chemical analyses, is principally to determine/verify the material nature of an analysed substance/material by the identification of one or more components or to assess whether the material product inclines to spontaneous ignition, whether it has pyrophoric properties, oxidizing abilities and the like with a sufficient result e.g. yes/no, false/true.

The above mentioned document [2] states that it is always considered how to apply the uncertainty of the measurement with qualitative tests. One of the accesses is the determination of the probability of wrongly expressed positive or negative results. An international working group was established for this purpose to prepare a relevant document.

A brief study in this field is the article of S. L. R. Ellison et al. [9]. It cites, among others:

- the qualitative chemical analyses can be understood as much more important than the quantitative ones which work with the presumption of the rightness of the identification of substances/materials, which are the subject of the quantification,
- the selectivity, the specificity, the detection limit, the falsely positive and the falsely negative assessment are relevant characteristics for interpreting qualitative results,
- it boots the term „the identification certainty" as a parameter quantifying the degree of the confidence of the following classification,
- it recaps publicized works shortly with the conclusion that the Bayes´ theorem provides a fair frame for the assessment of the uncertainty of the classification (designation), which is usually done on the basis of a qualitative test result,
- it cites an example of the application of this theorem in the forensic science e.g. for the identification of the type of blood, glass, DNA [14].

Further it mentions the fact that because the method is qualitative, its accuracy is not stated with it, and is the standard deviation of the results.

BAYE´S THEOREM

The author has already described the possibilities of the statistical valuation of quantitative results of laboratorial measurements/tests of the fire technical equipment and extinguishing agents for the need of the certification [10], [11]. The procedure is also applicable for the results of quantitative chemical analyses. It is possible to derive the primary relation of Bayes´ theorem according to equations (3) and (4) from known relations, see e.g. [15] for the conditional probability of the *H* hypothesis considering the *E* experiment/evidence, *P(H/E),* equation (1) and reversely the conditional probability of the E experimental evidence regarding the *H* hypothesis *P(E/H),* equation (2).

$$P(H/E) = \frac{P(H \cap E)}{P(E)} \tag{1}$$

$$P(E/H) = \frac{P(H \cap E)}{P(H)} \tag{2}$$

Where $P(H \cap E)$ is the probability of the penetration of the *H* hypothesis and *E* the experimental/evidence,

P(H) and *P(E)* are the unconditional so-called „a-priori" probabilities of the *H* hypothesis and the *E* evidence hypothesis and they are different from zero.

P(H/E) and *P(E/H)* are the conditional, „a-posteriori" probabilities.

$$P(H/E) = \frac{P(H) \cdot P(E/H)}{P(E)} \tag{3}$$

$$P(E/H) = \frac{P(E)\cdot P(H/E)}{P(H)} \quad (4)$$

When we express P(E) with the help of the known relation (5), it is possible to derive another practical form of the Bayes´ theorem by its substitution into the equation (3), see equation (6).

$$P(E) = P(H \cap E) + P(\bar{H} \cap E) = P(E/H).P(H) + P(E/\bar{H}).P(H) \quad (5)$$

where $\bar{H}$ is the supplement of the *H* hypothesis/event (opposite hypothesis/event) and it is true that the $P(\bar{H}) + P(H) = 1$

$$P(H/E) = \frac{P(H)\cdot P(E/H)}{P(H).P(E/H) + P(E/\bar{H}).P(\bar{H})} \quad (6)$$

The odds form of Bayes´ equation is also used practically, see equation (7).

$$\frac{P(H/E)}{P(\bar{H}/E)} = \frac{P(H)}{P(\bar{H})} \cdot \frac{P(E/H)}{P(E/\bar{H})} \quad (7)$$

where the fraction on the left side of the equation, $\frac{P(H/E)}{P(\bar{H}/E)}$ is the “a-posteriori” odds of the chances/ expectations of the H hypothesis regarding the E experiment (a-posteriori odds),

The fraction $\frac{P(H)}{P(\bar{H})}$ is the “a-priori” odds of the chances/ the fraction *H* regarding its negation (a-priori odds) and the term $\frac{P(E/H)}{P(E/\bar{H})}$ is the so-called likelihood ratio (*LR)*.

THE APLICATION OF BAYES´ THEOREM FOR THE NEED OF QUALITATIVE CHEMICAL AMNALYSES

The example of frequently occurring chemical analyses of samples from the seat of a fire for the content of accelerants (largely diesel oil (**DO**) and automobile petrol (**AP**)) for the confirmation or the negation of the arson hypothesis is chosen for the application of the above-mentioned relations from the illustrative by reason. The procedure of the assessment of the uncertainty of this hypothesis can be expressed by the next steps on the basis of the result of the tests:

Securing the inputting data – chemical composition of:

- **to AP** [12]:

Boiling range (°C): - (30 – 210)

The composition (% v/v):
- Olefin: max. 18, typically cca 10
- Aromates: max. 35, typically (30 – 35)
- from which benzene: max 1, cca 0,7
- Alcanes (n+i+cyklo): residue to100
- Characteristic analytes : Ethers (usually MTBE):
- max. 15 (may be ETBE) and Ethanol (bioethanol) max. 5,

- The general content of oxygen, % m/m: max. 2,7
- The general content of sulphur, mg/kg: max. 10

- **to DO** [12]:

Boiling range [°C]: (180 - 360)

The composition:
- Aromates (20 - 30), from which polyaromates max. 8 [% v/v],
- Saturated hydrocarbons (n+i+cyclo) = the rest up to 100, from which n-alkanes (10 - 25),

- Characteristic analytes: n-17/Pristane, n-18/Phytane, FAME (MEŘO): max. 7,
- The content of sulphur [$mg.kg^{-1}$]: max. 10.

SWS (Secondary Working Standard) was prepared from the unleaded petrol evaporated ex 75 % from the Restek solution. It can be generally stated that the characteristic sections of both fuels change by the vaporization of a sample, degradation changes and the presence of combustion products. Therefore, the interpretation of chromatograms requires experience. Further see Figure 1 and 2 and the Table 1 and 2.

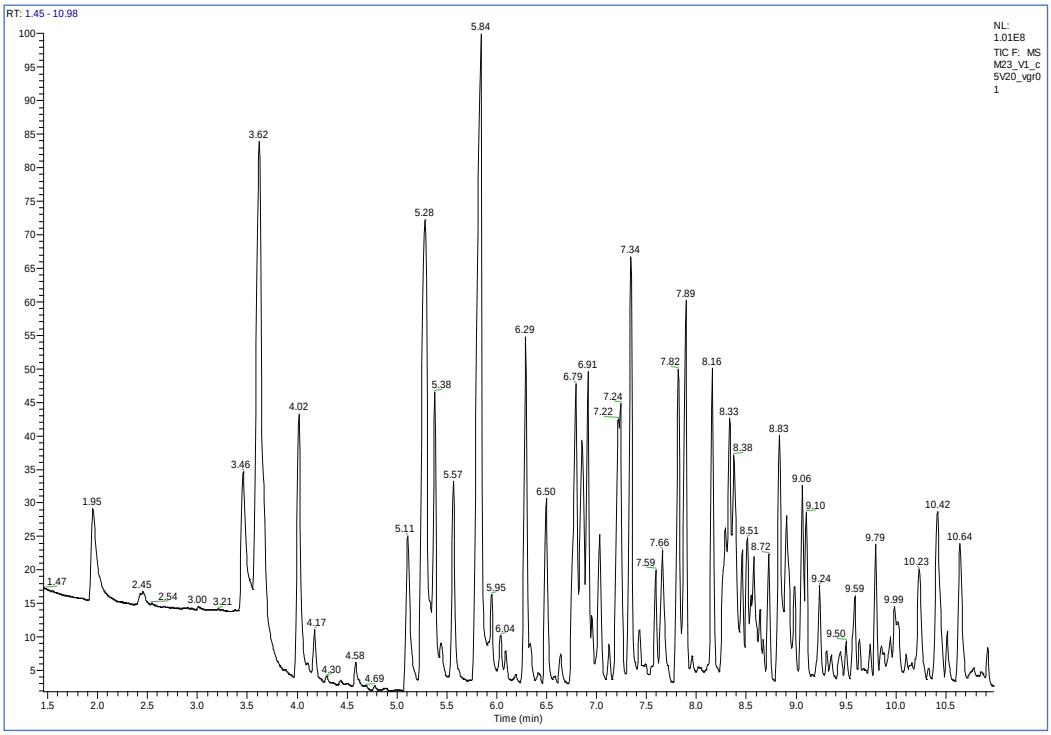

Fig. 1 - An example of the SWS pattern [13]

Tab. 1 - Characteristic components found by the GC- MS method in a SWS sample [13]

Retention time [min]	**Analyte name**
1,95	toluene
3,52	ethylbenzene
3,62	m-p-xylene
4,02	o-xylene
5,84	1,2,4 -trimethylbenzene
7,34	2- dimethyl-1-4-ethylbenzene
10,42	2- methylnaphtalene
10,64	1- methylnaphtatelene

Further see Figure 2 and the Table 2. It can be generally stated again that the characteristic sections of both fuels change by the vaporization of a sample, by its degradation changes, by the presence of combustion products. Therefore, the interpretation of chromatograms requires experience.

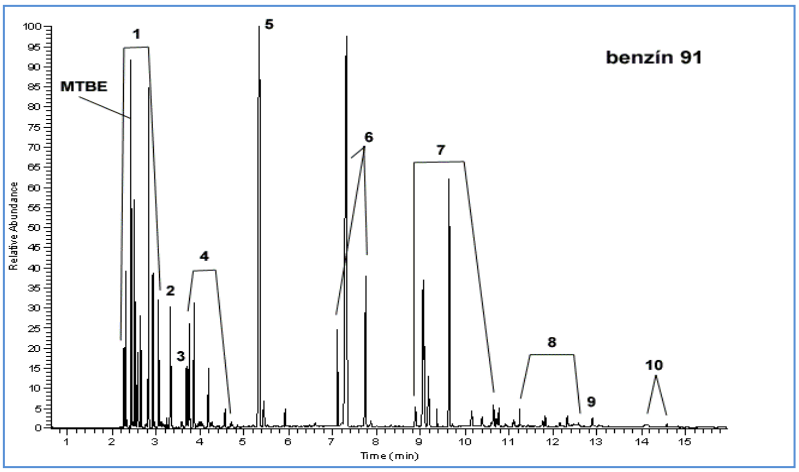

Fig. 2 - An example of the fresh automobile petrol pattern (GC - the straight forward spray of 0.3 µl of the sample [13]

Tab. 2 - Characteristic components found in a sample of the fresh automobile petrol by the GC-MS method [13]

Notation	Name of component
1, 3, 4	Group of C5-C8 saturated alkanes
MTBE	Terc-butyl-1methylether (CAS:1635-04-4)
2	Benzene
5	Toluene
6	Isomers of xylenes
7	Group of C3 alkyl benzenes
8	Group of C4 (C5) alkyl benzenes
9	Naphthalene
10	Isomers of 1Methyl Naphthalene
etc. (AP- totally approx. 300 - 400 components)	

The sensitivity, the detection limits for inquired substances, the linearity, the reproducibility and the selectivity of the applied method of the chemical analysis

The suitability of the SPME-GC / MS analytical procedure for the purpose was validated by a study that determined the analytical characteristics: sensitivity, detection limit, linearity, selectivity and repeatability. Terminology used:

Analyte: A sample component determined by analysis

Sensitivity: The concentration of the analyte that causes the response of measuring instrument (*S*) greater than three times the background noise level (*N*). It is given also by the correlation coefficient of the calibration lines as the square root of coefficient of determination, R^2

LOD: (Limit of Detection): the smallest analyte concentration that still causes the response of the measuring system to be recognizable from other influences with acceptable statistical confidence = $3\ h_n / m$ (baseline noise ratio and angular coefficient of a calibration line)

Linearity: Tightness of the match between the magnitude variable (peak height) and the independent magnitude (SWS analyte concentration). It is expressed by the angular coefficient of a calibration line, TIC (Total Ion Current) values versus analyte concentration

Repeatability limit: The value at which the probability of 95 % is assumed to be below or equal to the absolute value of the difference between the two test measurement results measured under repeatability conditions. It is expressed by the relative standard deviation (RSD)

Selectivity: **I**t is a sufficient distinguishment between individual peaks in TIC records[x]
x ... numerical expression of the peak area of the TIC record in electronic units determined by means of a chromatograph, X-calibur program.

Calibration: It was verified by calibration whether the response in the variously concentrated mixtures was linear. The SWS reference solution was applied to the layer of calcined sand in sheet metal containers in quantities: m_1; m_2 and m_3. After analysis of the two chromatograms mentioned above, calibration lines were plotted, see Figures 3 and 4, and the parameters listed in Table 3 were calculated for selected components.

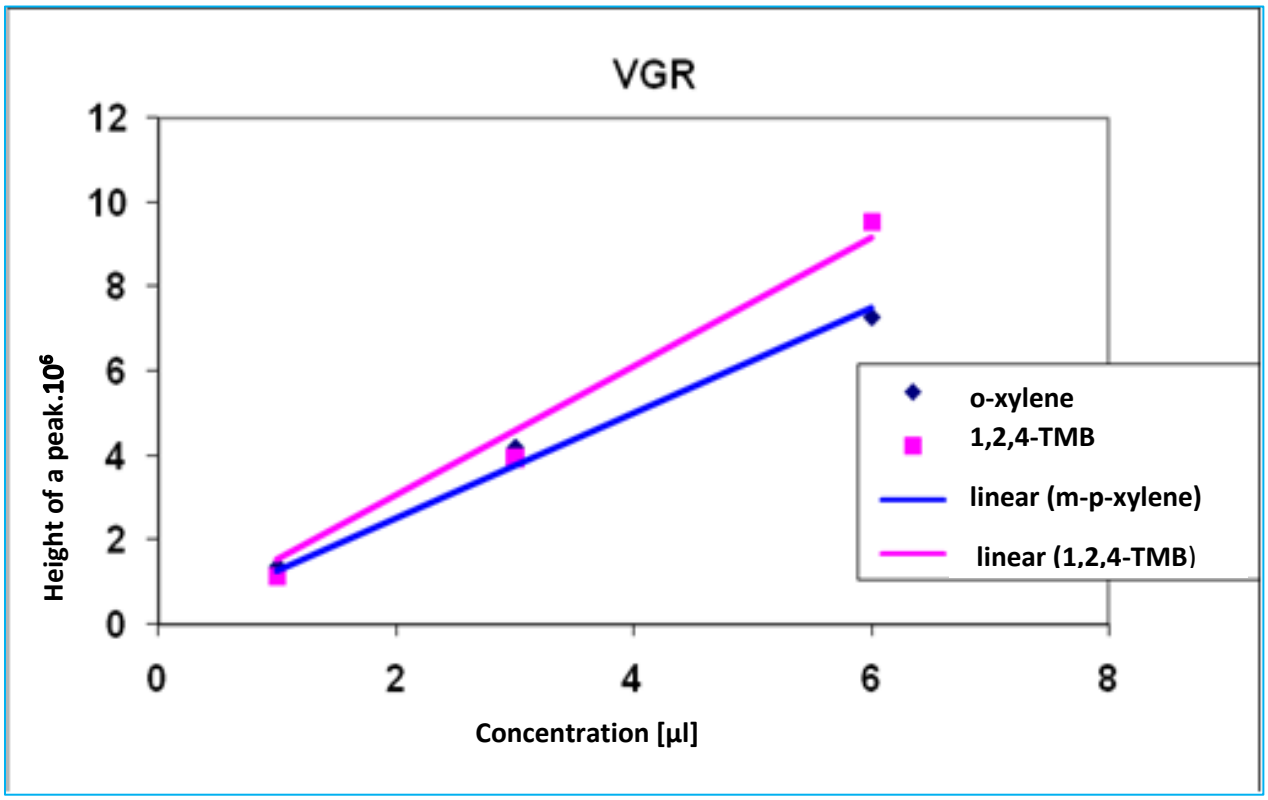

Fig. 3 - Calibration lines - Gas chromatograph GC 8000 Top with the mass spectroscopy MS: Voyager (Thermo Quest Finnigan) [13]

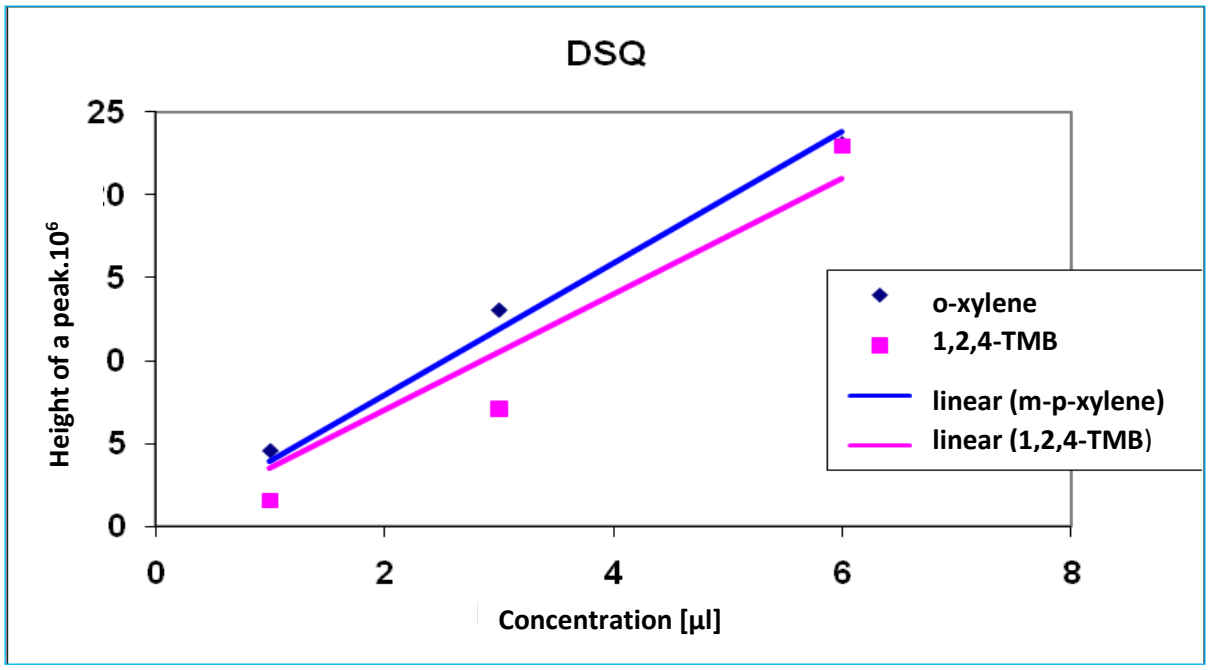

Fig. 4 - Calibration lines - Gas chromatograph GC Trace GC Ultra with the mass spectroscopy MS: DSQ II (Thermo Electron Corporation) [13]

With the GC/MS SPME technique, see Table 3.

Tab. 3 - The results of the validation measurement [13]

GC-MS	**VGR**		**DSQ**	
analyte / parameter	**o-xylen**	**1,2,4-TMB**	**m-p-xylene**	**1,2,4-TMB**
Sensitivity (R)	0,992	0,990	0,994	0,961
Detection limit (LOD)x	3801087	8144842	99404691	81662592
Linearity	1,253	1,525	3,962	3,4924
Repeatability limit, **r**	66467301	876281118	127900702	105034905

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The introduction of symbols and their definitions

Let us suppose that:

H is the presence of an analyte in a sample, the positive result,

$\bar{H}$ is the absence of a searched analyte in a test sample,

P(H) the *H* "a-priori" probability (before the test with the *E* evidence was realized with regard to *H* when the relation (8) holds true),

E the result of a test/chemical analysis (evidence),

P(E/H) the probability of the experimental evidence *E* with regard to *H.* If an experimental result is positive, this probability gets closer to 1. That is not the case if the measured concentration is in the proximity of the detection limit of an instrument/an analytical method. In that case it is advantageous to calculate the probability according to the equation (8):

$$P\,(E/H) = 1 - P(\bar{E}/H) \qquad (8)$$

When $P(\bar{E}/H)$ is the probability of a falsely negative result with regard to *H*,

$P(E/\bar{H})$ is the probability of a positive experimental result in the *H* absence (the falsely positive probability). The result is falsely negative in the case of the $P(\bar{E}/H)$

P(H/E) is the a-posteriori probability of the presence of an analyte in a test sample with regard to an experimental evidence, the E test result,
P(E/H) = 1 if the accelerant was found during an experiment. The exception is the case when the measured concentration of an analyte is in the proximity of a detection limit.

One can suppose for the interpretation of the Equation (3):
- when P(H/E) = 0.5, the probability of the rightness of the hypothesis is 50 %,
  = 0.99, the probability of the rightness of the hypothesis is certainly 99 %.

The next scale of values *P(H/E)* is designed for the interpretation of the results according to the equation (6):
<0.5 the hypothesis of the arson is irrelevant,
0.5 the hypothesis of the arson is not confirmed or disproved,
>0.5 and ≤ 0.7 the hypothesis of the arson is probable,
>0.7 and ≤ 0.8 the hypothesis of the arson is highly probable,
>0.8 the hypothesis of the arson is certainly relevant.

EXAMPLES OF THE CALCULATION AND THE INTERPRETATION OF THEIR RESULTS

According to the equation (6)

Input data based on author's experience and computing results are mentioned in Table 4.

Tab. 4 - The calculation of the P(H/E) on the basis of the result of a chemical analysis of a fire sample

P(H)	***P(*** $\bar{H}$ ***)***	***P(E/H)***	***P (E/*** $\bar{H}$ ***)***	$P(\bar{E}/H)$	***P(H/E)***
0,5	0,5	0,99	0,03	0,01	0,97
0,95	0,05	0,99	0,03	0,01	0,98

Results can be interpreted with the high justification certainty of the hypothesis of the arson in both cases. If the probability of the a-priori hypothesis P(H) is increased to 0.95 (e.g.

because the sample was taken in the place where a trained/certified dog signed it), the certainty of the rightness of the hypothesis rises too.

According to the equation (7)

After the substitution of data according to Table 4 the values at first case are

$$\frac{P(H/E)}{P(\bar{H}/E)} = (0{,}5\ /0{,}5)\ .\ (0{,}99/0{,}03) = 1\ .\ 33 = 33,$$

and at a second case:

$$\frac{P(H/E)}{P(\bar{H}/E)} = (0{,}95\ /0{,}5)\ .\ (0{,}99/0{,}03) = 1{,}9\ .\ 33 = 62{,}7$$

It is possible to interpret the results in the way that the hypothesis of the arson is relevant/has been confirmed in the first and the second case. This conclusion supposes that a combustible liquid identified as an accelerant was not used or stored in accordance with the operational regulations and/or by the evidences of responsible persons/witnesses in the given space.

CONCLUSION

Bayes´ theorem and its possible forms of the formulation are also usable for the fire science and fire technical expertise with the help of the “a-posteriori” probability of a verified hypothesis/event, the “a-posteriori” odds, chances/expectations of the H hypothesis with regard to the E experiment and the likelihood ratio which can be estimated on the basis of the results of the used qualitative validated tests/measurements/chemical analyses.
It can be supposed that they will be exploited expertly in the same way as with the evaluation of the uncertainties of the quantitative results of the tests/measurements, when checking the quality of production, etc. also in the field of a fire safety of buildings in the Czech Republic. It relates not only in qualitative analyses of building materials / products, e. g, by FTIR, but also in the probability risk assessment, e.g. for updates of the properties and reliability estimates of building materials and structures [16] - [20].

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