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Simultaneous determination of molybdenum(VI) and tungsten(VI) and its application in elemental analysis of polyoxometalates

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Abstract

Spectrophotometric determination of molybdenum(VI) and tungsten(VI) with application of Artificial Neural Networks is proposed and it was applied for elemental analysis of solid polyoxometalates. Better results in comparison with previously those achieved by previous published method were demonstrated. MALDI–TOF Mass Spectrometry was tested for possible determination of molecular weight of polyoxometalates utilizing different matrices. Phenomena observed during desorption–ionisation processes are discussed. LDI–TOF MS was found to be suitable for the determination of Mo:W ratio in polyoxometalates as a rapid screening method to follow synthetic procedure.

Keywords: Polyoxometalates; Simultaneous spectrophotometric determination; Molybdenum(VI); Tungsten(VI); Artificial Neural Networks; MALDI–TOF MS

1. Introduction

Polyoxometalates (POMs) are mostly polynuclear compounds concerning also other elements of Periodic Table (P, As, Sb, Si, etc.) in minor amount [1–6]. POMs form a unique class of mostly water-soluble compounds with highly symmetrical structure and charge ranging from −3 to −14 [1–6]. The majority of POMs are composed of polyhedron structural cavities which are capable of encapsulation of alkali metal, alkali earth, transition metal, lanthanide and actinide ions [1–26]. For their interesting chemical properties, the POM's are employed in wide range of applications in recent years, e.g. in catalysis, photochemistry, material science and medicine as inorganic drugs [27–29].

Due to high molecular weight of POMs and some potential difficulties in course of chemical analysis, the composition of POMs should be verified, if possible, by several techniques. A potential analytical method should be able to distinguish between very similar formulations (e.g. $P_2W_{17}O_{61}{}^{10-}$ versus $P_2W_{18}O_{62}{}^{6-}$) and also the sufficient precision in order to determine the heteroelements of low abundance (<1–2%) [21]. POMs containing tungsten and molybdenum are decomposed in alkaline media with simultaneous formation of simple tungstate and molybdate which can be determined by laborious, time consuming gravimetric [21,30], titrimetric [21,31] or colorimetric procedures [21,30,32]. In order to eliminate several cations interfering in analytical procedure, determination by molecular absorption spectroscopy combined with extraction [21,33] or a technique based on precipitation with α-benzoinoxime [34] were proposed. In addition, some instrumental analytical techniques such as electroanalytical (polarography [21,35,36]) and atomic spectroscopical (ICP [30,37]) were utilized for the determination of molybdenum and tungsten content in POMs. Major limitation of ICP–AES and even also molecular spectroscopy is associated with potential interelemental interferences [30,37]. Some of the mentioned techniques (e.g. polarography, cyclic voltammetry, Raman spectroscopy in H_2O, infrared spectroscopy in D_2O, ^{183}W NMR spectroscopy) are useful for "fingerprint characterization", mainly differentiation of isomers [21]. For the colorimetric analysis, the *o*-diphenolic derivatives as suitable reagents were proposed for the molybdate and tungstate determination [38–41]. Tiron, i.e. disodium salt of 1,2-dihydroxybenzene-3,5-disulfonic acid (catechol-3,5-disulfonic acid), can be used as a common analytical reagent in colorimetric procedure measuring absorbance of a product of stoichiometry 1:1 at wavelength 370–380 nm under experimental conditions

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(phosphate buffer, pH = 6.8, $c_L \geq 10\, c_M$ [39–41]). Analogous experimental conditions were proposed independently in a later work [32].

In order to overcome the influence of ions interfering the determination, application of matrix matching procedure (correction of the measured analytical signal) [30,37] or some advanced chemometric techniques (e.g. PLS, ANN) involving the interferences causing non-linearities of analytical signal into calibration process can be proposed. The basic concept of Artificial Neural Networks (ANNs) was developed about 50 years ago [42–44], however the interest of scientists increased with the introduction of new model of ANNs using probabilistic transfer function and error back-propagation algorithm with conjunction of the fast progress of computer technology in eighties in all branches of science (e.g. chemistry, biology, pharmacy, etc.). ANNs as so called "soft-model" techniques can predict properties without any knowledge of chemical, thermodynamic and/or mathematical models (functional relationships) [42–44] and therefore can be used also for evaluation of results from analytical measurements. Nowadays, ANNs are utilized in some branches of analytical science, e.g. for calibration of ion-selective electrodes [45,46], evaluation of equilibrium [46] or rate [47,48] constants from experimental data, optimization of analytical methods [49], etc.

Matrix-assisted laser desorption–ionisation–time of flight mass spectrometry (MALDI–TOF MS) is a method well known as a powerful tool for the determination of the molecular weight of biomolecules, such as peptides, proteins or oligonucleotides. Its applications in inorganic analysis are not very frequent, the analysis of some clusters was very recently described [50–53]. In case of POMs, the possibilities of the method have not already been described in the literature. Only one similar case concerning molybdenum oxide giant spheres has been examined until now [54,55]. Here, *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB) was found as a suitable matrix for the generation of molecular ions of these compounds. Mass spectrometric properties of isopolyoxometalates have already been examined only by ESI–MS, where complex decomposition mechanisms were monitored for molybdate [56] and tungstate [57].

In this paper, we have studied the possibility of application of ANNs for the simultaneous determination of molybdenum and tungsten in POM samples by means of molecular spectroscopy measuring the intensity of coloured product formed by reaction of molybdate/tungstate with chromogenic organic reagent (Tiron). In addition, the possibility of MALDI–TOF MS for analysis of POMs samples in order to determine their molecular weight and composition was investigated and the results of both new methods are compared.

2. Experimental

The absorbance measurements were carried out on double-beam spectrophotometer UV-2 (Pye Unicam, UK). The pH of all measured solutions was checked by means of combined glass electrode (Monocrystaly Turnov, Czech Republic) joined with pH-meter OP-208 (Radelkis, Hungary).

Mass spectra measurements were carried out on Axima-CFR from Kratos Analytical, Shimadzu Group Company (Manchester, UK), equipped with nitrogen laser wavelength of 337 nm obtained from Laser Franklin Inc. (MA, USA). Matrices α-cyano-4-hydroxycinnamic acid (CHCA), 2,5-dihydroxybenzoic acid (DHB), dithranol (DIT) and 3-hydroxypicolinic acid (3-HPA) were obtained from Sigma–Aldrich (Steinheim, Germany) and *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB) from Fluka (Buchs, Switzerland). For LDI–TOF MS experiments, 1 μl of aqueous POM solution was applied on the sample plate and allowed to

Table 1
The results of multicomponent analysis of molybdate and tungstate in artificial samples by means of ANN

Content given (Mo/W mg l^{-1})	Content found (mg l^{-1})							
	Mo				W			
	0th der. data[b]	1st der. data[c]	2nd der. data[d]	Combined data[e]	0th der. data[b]	1st der. data[c]	2nd der. data[d]	Combined data[e]
4.00/24.00	3.89 (−2.75)*	4.03 (+0.75)*	4.03 (+0.75)*	3.88 (−3.00)*	24.05 (+0.21)*	23.54 (−1.92)*	23.59 (−1.71)*	23.73 (−1.13)*
4.00/32.00	4.04 (+1.00)	3.89 (−2.75)	4.02 (+0.50)	3.88 (−3.00)	31.92 (−0.25)	31.63 (−1.16)	31.70 (−0.94)	31.56 (−1.38)
6.00/16.00	6.07 (+1.17)	5.66 (−5.67)	5.85 (−2.50)	6.06 (+1.00)	16.24 (+1.50)	15.82 (−1.13)	15.82 (−1.13)	15.77 (−1.44)
8.00/0.00	7.81 (−2.38)	7.95 (−0.62)	7.96 (−0.50)	7.94 (−0.75)	0.11 (–)	0.07 (–)	0.12 (–)	0.16 (–)
8.00/16.00	7.86 (−1.75)	7.96 (−0.50)	7.98 (−0.25)	7.97 (−0.38)	16.12 (+0.75)	16.27 (+1.69)	16.14 (+0.88)	15.88 (−0.75)
4.00/40.00	4.08 (+2.00)	3.90 (−2.50)	3.91 (−2.25)	3.95 (−1.25)	39.37 (−1.58)	39.99 (−0.02)	39.82 (−0.45)	40.06 (+0.15)
3.00/28.00	3.03 (+1.00)	2.96 (−1.33)	2.98 (−0.67)	3.02 (+0.67)	28.06 (+0.21)	27.86 (−0.50)	28.12 (+0.43)	27.95 (−0.18)
5.00/20.00	5.02 (+0.40)	4.93 (−1.40)	4.98 (−0.40)	4.96 (−0.80)	20.31 (+1.55)	19.92 (−0.40)	20.09 (+0.45)	20.03 (+0.15)
7.00/10.00	7.09 (+1.29)	7.10 (+1.43)	7.08 (+1.14)	6.86 (−2.00)	9.64 (−3.60)	9.98 (−0.20)	9.89 (−1.10)	9.76 (−2.40)
Average rel. error	+0.00 (+1.53)[a]	−1.40 (+1.88)[a]	−0.46 (+1.00)[a]	−1.06 (+1.43)[a]	−0.15 (+1.21)[a]	−0.45 (+0.88)[a]	−0.45 (+0.88)[a]	−0.87 (+0.95)[a]

*Relative error (%).
[a] Calculated from absolute values.
[b] ANN architecture (201:5:2).
[c] ANN architecture (199:4:2).
[d] ANN architecture (197:3:2).
[e] ANN architecture (597:2:2).

Table 2
The results of analysis of polyoxometalates samples obtained by two spectrophotometric procedures

Sample (POM)	Theoretical content (%)		Stoichiometric ratio	Old spectrophotometric method (%) [32]		New spectrophotometric method (%)	
	Mo	W	Mo/W	Mo	W	Mo	W
$K_8SiMoW_{10}O_{39}.13H_2O$	3.06	58.68	0.100	2.89 (−5.56)[a]	59.76 (+1.84)[a]	3.02 (−1.31)[a]	58.10 (−0.99)[a]
$K_8SiMo_2W_9O_{39}.13H_2O$	6.30	54.34	0.222	6.12 (−2.86)	55.16 (+1.51)	6.20 (−1.59)	53.86 (−0.88)
$K_8SiMo_3W_8O_{39}.13H_2O$	9.73	49.74	0.375	9.56 (−1.75)	48.87 (−1.75)	9.72 (−0.10)	49.29 (−0.90)
$K_8SiMo_4W_7O_{39}.13H_2O$	13.38	44.85	0.571	12.38 (−7.47)	46.73 (+4.19)	13.10 (−2.09)	44.00 (−1.90)
$K_8SiMo_5W_6O_{39}.13H_2O$	17.25	39.66	0.833	15.50 (−10.14)	40.50 (+2.12)	17.23 (−0.12)	39.30 (−0.91)
$K_8SiMo_6W_5O_{39}$	23.41	37.38	1.200	21.11 (−9.82)	38.85 (+3.93)	23.32 (−0.38)	36.40 (−2.62)
$K_8SiMo_7W_4O_{39}$	28.32	31.01	1.75	27.56 (−2.68)	31.40 (+1.26)	28.04 (−0.99)	30.97 (−0.13)
$K_8SiMo_8W_3O_{39}$	33.61	24.15	2.667	30.28 (−9.91)	25.99 (+7.62)	32.79 (−2.44)	23.99 (−0.66)
$K_{11}Eu(PMo_3W_8O_{39})_2.28H_2O$	9.74	49.75	0.375	8.97 (−7.91)	51.30 (+3.12)	9.37 (−3.80)	49.58 (−0.34)
$K_{11}Eu(PMo_5W_6O_{39})_2.28H_2O$	17.25	39.67	0.833	16.56 (−4.00)	39.63 (−0.10)	16.95 (−1.74)	38.40 (−3.20)
$K_{13}Eu(SiMo_8W_3O_{39})_2.28H_2O$	30.07	21.60	2.667	30.15 (+0.27)	21.72 (+0.56)	30.30 (+0.76)	21.65 (+0.23)
Average relative error	–	–	–	−5.62 (+5.67)[a]	+2.21 (+2.54)[a]	−1.25 (+1.39)[a]	−1.12 (+1.16)[a]

[a] Relative error (%) calculated from absolute values.

dry in an air stream at room temperature. For MALDI–TOF mass spectrometric analysis, two different sample preparation techniques were used: (i) matrix solution in 0.1% TFA:acetonitrile 1:1 (v/v) in the volume of 1 μl was mixed with 1 μl of the sample solution in water:acetonitrile 1:1 (v/v) by pipetting up and down directly on the sample target and allowed to dry in an air stream; or (ii) the sample solution was applied on dry layer of matrix crystals. Analyses were carried out under 10^{-4} Pa pressure in positive or negative modes and both in linear and reflectron arrangements.

The analytical procedure of spectrophotometric determination of molybdenum(VI) and tungsten(VI) in mixtures was used as described elsewhere [32]. The samples weighing 20.0 mg of POM's were decomposed in alkaline media to form simple molybdate and tungstate ions [31] and then determined as coloured complexes formed by reaction with Tiron at pH = 7.00 [32,41]. Each spectrophotometric analysis was repeated at least twice in order to ensure the robustness of proposed method.

Sodium tungstate (Fluka, Switzerland), sodium molybdate (Lachema, Brno, Czech Republic) and Tiron (Lachema, Brno, Czech Republic) were of analytical grade and used as received. All solutions were prepared dissolving substances in bidistilled water. The heteropolyoxometalates (see Table 2) were prepared using experimental procedures described in literature [15–24] and characterized by thermogravimetry, differential thermal analysis, IR and Raman spectroscopy [22].

The experimental spectrophotometric data were exported into EXCEL™ and then analysed by Back-propagation multilayer Artificial Neural Network using Trajan™ (StatSoft, UK) software. Absorbances in wavelength region 350–550 nm with increment 1 nm (totally 201 input neurons) were used as input data in case of normal spectra and/or less in case of derivative spectra and concentrations of molybdate and tungstate as output neurons. For each chemical system the optimal architecture was searched using training (13 solutions) and verification set (6 solutions) in concentration region 0–8 mg l^{-1} (Mo) and 0–32 mg l^{-1} (W). The concentrations of mixture solutions for search of optimal ANN architecture were proposed according to central composite experimental design [58]. The parameters for ANN training were following: activation function linear, number of learning epochs 1000, learning rate 0.6, momentum 0.3. Optimal ANN with the correct number of hidden neurons (see Fig. 1 as example) was applied for prediction of both tungstate and molybdate concentrations in unknown samples and POMs from absorbance data. The first and second derivative spectra were calculated according to Savitzky–Golay procedure using second polynomial formula for five points [58–61].

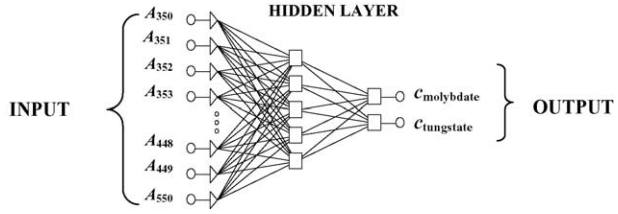

Fig. 1. Example of optimal architecture of ANN (201:5:2) for simultaneous determination of molybdate and tungstate in mixtures.

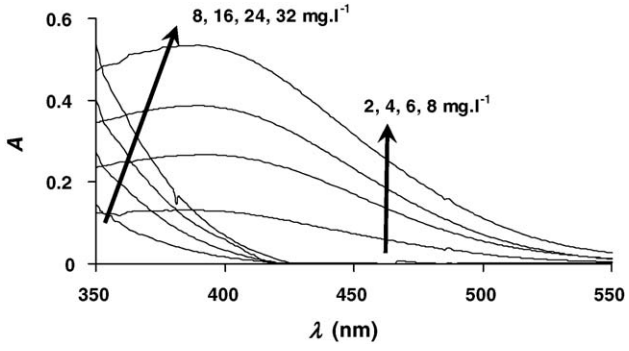

Fig. 2. Absorption spectra of the molybdenum and tungsten complexes with Tiron (1.6% m/m solution, pH = 7.00).

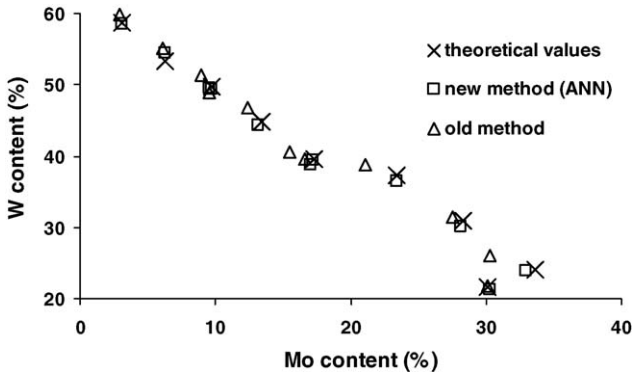

Fig. 3. Comparison of two analytical procedures employed for simultaneous determination of content of molybdenum and tungsten in samples of POMs.

3. Results and discussion

3.1. Spectroscopic analysis

Analytical method for simultaneous multicomponent analysis of molybdenum and tungsten in POMs was taken from the literature [32]. Chemical reaction of molybdate and tungstate with Tiron forming coloured products was utilized for their determination. The molybdate forms coloured product with absorption band maximum about wavelength 390 nm while coloured product of tungstate has absorption band maximum in UV wavelength region (Fig. 2). Anyway, for the spectrophotometric determination of tugstate and molybdate in their mixtures, it is necessary to consider the relative interference for determination which can lead to a systematic error. This effect can be involved also in calibration process as it was demonstrated [32]. In the next step, the use of ANN's was tested for calibration and prediction of concentrations for both analytes in mixtures. The method was firstly verified for synthetic mixture samples (Table 1). It can be seen from results for normal spectra that average relative error does not exceed 2% for both analytes.

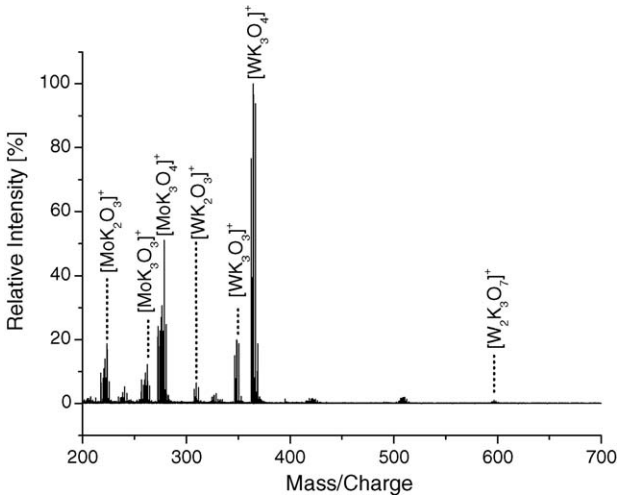

Fig. 5. LDI–TOF mass spectra of $K_8SiMo_8W_3O_{39}$, measured in reflectron positive mode with pulsed extraction and laser power 4.3 mW.

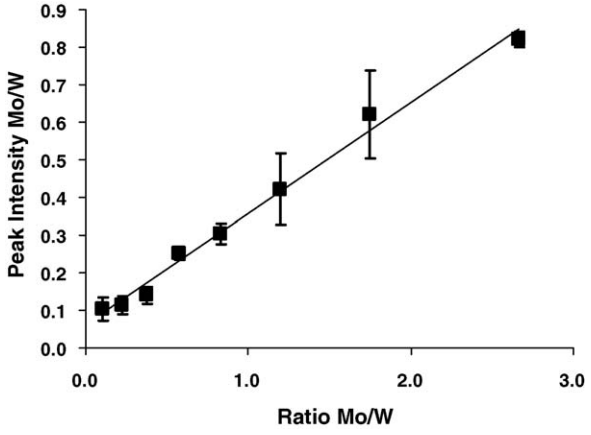

Fig. 6. Correlation between integral peak intensities of isotopic patterns and ratio Mo/W in POM's. From the mass spectra, intensities of dominant peaks of three molybdenum and two tungsten containing ions were accumulated and divided $(I_{MoK_2O_3} + I_{MoK_3O_4} + I_{MoK_3O_3^+})/(I_{WK_3O_3} + I_{WK_3O_4^+})$.

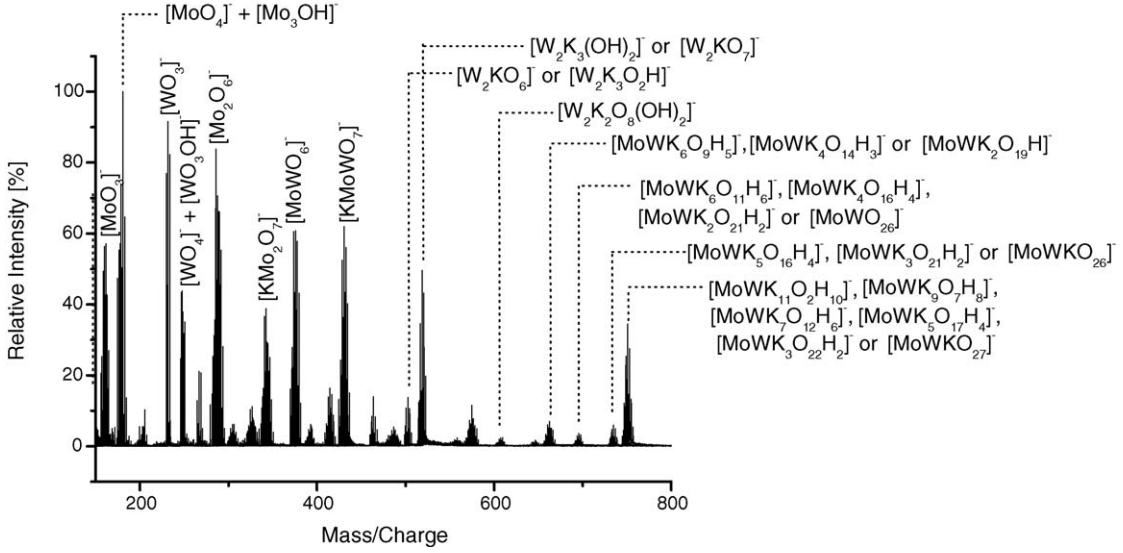

Fig. 4. LDI–TOF mass spectra of $K_8SiMo_8W_3O_{39}$, measured in reflectron negative mode with pulsed extraction and laser power 3.6 mW.

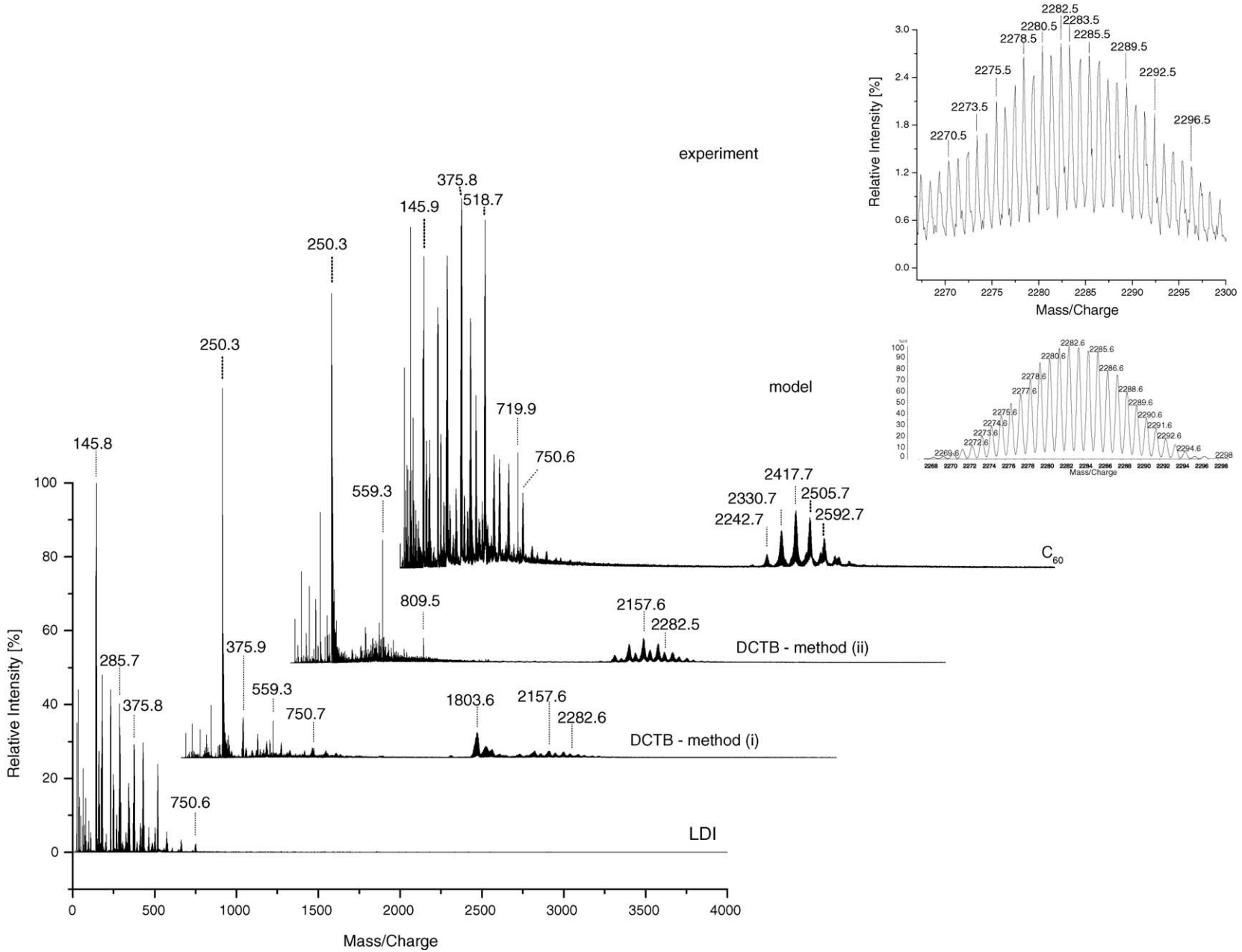

Fig. 7. Comparison between mass spectra of $K_8SiMo_8W_3O_{39}$ measured without matrix (LDI) and with DCTB or C_{60} as matrices (two different sample preparation protocols were used in case of DCTB, c.f. Section 2). Reflectron negative mode with pulsed extraction and laser power in case of LDI 3.6 mW, for DCTB 2.3 mW and for C_{60} 3.0 mW.

Applying mathematical procedure of deriving analytical signals, improvement of calculated parameters for the determination of stability constants from spectroscopic data [62,63] and/or resolution of overlapping peaks in CZE was demonstrated [64]. Using derivative spectra as input in ANN, the average relative error for the calculated concentrations does not change so significantly (Table 1) and also the combination of normal and derivative spectra made no improvement, as well.

Real samples of POMs were analyzed by a new method using ANN of optimal architecture (Table 2). Since some POMs contain also silicon, phosphorus and europium(III), it was verified whether presence of these interferents does have influence on predicted values of concentrations by ANN. The limit concentrations ($mg\,l^{-1}$) are 400 (P as Na_3PO_4), 2.5 (Eu as $EuCl_3$) and 50 (Si as Na_2SiO_3) and the results are in accordance with those found in the literature [32]. For comparison, the results of analysis obtained by an old spectrophotometric method [32] are given in Table 2. Generally, applying ANN, the average relative error for the content of tungsten and molybdenum determined in POM's decreased significantly (about 1% as average relative error). Also the accurate results obtained by the old method depend on molybdenum content in POMs and it can be noticed that relative error increases with higher molybdenum content (Table 2; Fig. 3). It is interesting that this is not observed when ANN is applied.

3.2. MALDI–TOF MS analysis

In some cases, compounds do not require the presence of matrix for the generation of molecular ions. Therefore, in the first step, the possibilities of LDI–TOF mass spectrometric analysis of POM's were examined. After exceeding laser power of 3.0 mW, either positively or negatively charged species were detected. The comparison of $K_8SiMo_8W_3O_{39}$ spectra obtained in positive or negative detection modes is given in Figs. 4 and 5. Several cluster species resulting from laser-induced decomposition of the compounds were detected. Isotopic patterns of POM peaks allow the determination of the number of particular metal atoms in the species. It follows from mass spectra interpretation that some signals cannot be unambiguously identified, as more species with equal molecular weight and very similar isotopic patterns are fitting the peaks. However, one could follow the structure of the original molecules to determine the stoichiometry of the fragments, but it is evident that highly complex recombination processes take place during LDI.

Interestingly, all examined POMs including those that contain europium atom yield the same fragments, the difference in their LDI–TOF mass spectra is only in peak intensities. The intensities depend on the content of molybdenum and tungsten atoms in the original molecules. The relationship of the ratio of dominant peak intensities of isotopic patterns corresponding to the presence of particular metals as function of the Mo:W ratio is shown in Fig. 6. These experimental points were fitted by linear non-weighted regression and the regression line $Y = (0.29 \pm 0.01)X + (0.063 \pm 0.015)$ with correlation coefficient 0.9951 was obtained. It can be seen that the standard deviation of each value in this dependence is too high to allow the precious determination of Mo:W ratio in the molecules from their LDI–TOF MS spectra. On the other hand, mostly for high Mo:W ratio, LDI–TOF MS might serve as a rapid screening method for the estimation of their abundance in the molecules. The fragment peaks can be observed in 0.01 $g\,l^{-1}$ solutions of POMs in both modes. This means that using 1 μl sample deposition, about 4 pmols of these compounds can be detected using LDI–TOF MS technique.

However, the information about the POM molecular weight is not provided by LDI ionization technique. Therefore, finding a matrix suitable for the generation of POM molecular ions was the next step. Besides four most frequently used matrices (DHB, CHCA, 3-HPA and DIT), several other potential matrices have been examined. Besides previously reported DCTB, we also tried fullerene C_{60}, which has shown matrix-like properties protecting uranyl from laser-induced photochemical reactions [65], nano-cobalt and sulphur.

Fig. 7 shows comparison between MALDI–TOF mass spectra of $K_8SiMo_8W_3O_{39}$ using DCTB and C_{60} as matrices. In can be seen that DCTB is capable of generating of POM molecular ions. They are shown in detailed frame, compared with a theoretical model, calculated from natural abundance of the elements. Beside these signals, several other peaks appeared, showing that DCTB matrix effect is not sufficient enough to protect POMs from undesired photochemical reactions induced by the laser pulses. Using DCTB allows the detection of 4 pmols of $K_8SiMo_8W_3O_{39}$ (similarly to LDI), while decreasing the number of molybdenum atoms in the analyte results in worse MALDI–TOF mass spectrometric detection limits. It is also interesting to see how the sample preparation procedure influences the nature of the mass spectra. It seems that longer contact between the analyte and the matrix, which takes place when they are dried together, results in some POM partial decomposition. Also, here the presence of europium atom does not influence the nature of the POM MALDI–TOF mass spectra, as e.g. $K_{11}Eu(PMo_3W_8O_{39})_2{\cdot}28H_2O$ and $K_8SiMo_3W_8O_{39}{\cdot}13H_2O$ spectra are very similar.

Fullerene C_{60} provides peaks that according to isotopic patterns correspond to POM ions, but their molecular weight is shifted by +263 Da. Here, C_{60} probably does not act as a "true" matrix, as it is not present in the mixture in a high matrix-to-analyte molar ratio. Additionally, peaks known from LDI spectra of POMs appeared also in the mass spectra showing that C_{60} does not protect the analyte from undesired photo-induced decomposition. Matrices CHCA, DHB and 3-HPA show very weak signals of analyte that correspond to those obtained from DCTB. Other examined matrices did not yield any molecular or pseudo-molecular peaks of POM's.

4. Summary

The new spectrophotometric procedure followed by ANN evaluation of experimental data was proposed for the multicomponent analysis of molybdate and tungstate. The application of the first and second derivative spectra and their combination does not show improvement of results. The new analytical procedure was utilized for POMs of various composition. The method

gives more accurate results of analysis (maximal relative error for molybdenum is lower than 4% and for tungsten 3%) than older method [32] using calibration curve. Taking into account average relative error, the improvement can be characterized by factor about 5 for molybdenum and about 2 for tungsten.

Possibilities of LDI/MALDI–TOF mass spectrometric analysis of POMs have been examined. DCTB was found to be the most suitable matrix, nevertheless yielding besides the molecular peak several other fragment ions. Mass spectrometry was found as a rapid screening method for the estimation of Mo/W stoichiometric ratio in various POM compounds. Our work is the first systematic study of processes taking place in POMs under laser action. The observed phenomena are very complex and they would be studied in more detail to improve the possibility of application of LDI/MALDI–TOF mass spectrometric analysis of POMs.

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