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Molecular speciation of inorganic mixtures by Fourier transform laser microprobe mass spectrometry

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Abstract

Speciation analysis of as-received solids and micro-objects with the specificity of molecular instead of atomic or functional group information is increasingly needed. Fourier transform laser microprobe mass spectrometry (FT LMMS) is the only method capable of detecting signals referring to the intact analyte (molecular speciation) with the analytical specificity of high mass resolution. Although the methodology has been shown to be unique for identification of constituents in micro-objects and microscopical spots at the surface, its potential for quantitative analysis is often questioned. This paper demonstrates that the step from molecular identification towards semi-quantitative characterisation of local mixtures largely depends on the preparation of suitable reference samples for the calibration of the signal intensities as a function of the local concentration. The experimental methodology elaborated has been verified for mixtures of binary salts and oxysalts including the case of fine speciation, i.e., analytes with the same elements in different oxidation states. The empirical calibration functions allow the local analyte concentration to be determined within 3–10%, which is considered to be adequate for a variety of material science applications at the microscopical level.

Keywords: Fourier transform laser microprobe mass spectrometry; Molecular speciation; Inorganic salts; Semi-quantification

1. Introduction

Progress in material science and technology requires analytical chemistry to develop methods capable of determining the chemical composition in microvolumes of solids and in micro-objects. As the material properties and behaviour depends on the physico-chemical interactions between its components and the ones of the environment, the elemental composition is not longer sufficient and analytes must be characterised by means of molecular information. Amongst the current microprobes laser microprobe mass spectrometry (LMMS) and static secondary ion mass spectrometry (S-SIMS) are of particular interest [1,2]. Both methods are capable of detecting structural fragments and adducts of the intact analytes from both inorganic and organic surface constituents. The information depth of FT LMMS is 10 nm and that of S-SIMS is a monolayer. Unlike S-SIMS, LMMS is not hampered by charge build-up of insulating samples whereas the Fourier transform LMMS instruments allow the analytical specificity of ultra-high mass resolution to be exploited. The latter is required as solid state analysis does not allow chemical separation of

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the components to be achieved in, e.g., hyphenated chromatographic methods. Hence, the recorded mass spectrum becomes a complex superposition of data from many analytes. Identification of individual analytes requires separation of isobars as well as accurate determination of the elemental composition of the ions, in particular for organic compounds.

The LMMS methodology uses a focused UV laser with a spot diameter of 1–5 μm to evaporate and ionise analytes from a solid microvolume at power densities of 10^6–10^{10} W cm^{-2}. At first view, LMMS looks reminiscent to the so-called laser-induced mass spectrometric (LIMS) methods, that are capable of elemental analysis at the trace level [3]. However, the difference in irradiation conditions as to wavelength, pulse length, spot size and the time domain of the mass analyser used makes LIMS and LMMS quite different as to the information obtained and the application area. The analytical versatility of the initial time-of-flight (TOF) LMMS [4,5] has led to the development of various instruments by either improving the laser system or by implementing other types of mass analysers. Use of larger spots aims at better sensitivity and reproducibility [6], tuneable dye-lasers allowing resonant desorption–ionisation (DI) to be achieved improve detection limits and specificity [7] while (non)-resonant post-ionisation allow laser-desorbed neutrals [8] to be used analytically. Coupling the laser ionisation to different types of mass analysers has been explored by implementing quadrupoles [9], ion traps [10] and Fourier transform (FT) analysers [11–14]. Recently, LMMS led to the development of so-called aerosol TOF MS technology, allowing chemical analysis to be achieved on suspended particles [15,16]. In particular FT LMMS offers unsurpassed capabilities to identify analytes as it is the only instrument offering micro-analytical sensitivity in combination with high mass resolution (routinely above 100,000) and mass accuracy (routinely better than 1 ppm). As a result, the methodology is exploited for the molecular identification of unknown analytes (organic and inorganic) at the surface of micro-objects in a variety of material applications, e.g., aerosol research, detection of contaminants during material manufacturing and processing, etc. [17]. For such applications, it is often sufficient to know an estimate of the local concentration as opposed to an ultra-precise determination. Furthermore, by restricting the sampled volume, mass spectrometry becomes essentially confined to the detection of major components. As materials tend to be heterogeneous on the microscopic scale, trace constituents on a bulk scale are often major components on a local scale.

The step from the qualitative to the quantitative application of the LMMS methodology is generally considered as difficult, in particular because of its spot size between 1 and 5 μm [1]. Application of less focused lasers, irradiating a spot of 150–200 μm on the sample, allowed Kuzuya et al. [9] to quantify the Zn content between 5 and 10% in brass with a relative standard deviation on replicate experiments within 1%. To the best of our knowledge, the study of Allen et al. [6] has been the only one to deal with the quantification of molecular adducts from inorganic oxides. A TOF MS with a laser spot of 160 μm has been used. The intensities of the As_2O_3 and As_2O_5 adducts with AsO^- and AsO_2^- allowed the local mixture composition to be monitored using empirical calibration functions. The functions have different forms for the AsO^- and AsO_2^- adducts.

In our experience, the use of micro-analytical spots of 1–5 μm severely aggravates the step towards semi-quantitative speciation analysis. Specifically, the preparation of standards from a variety of molecular solids (not alloys) with a strictly reproducible composition within each analysed micro-volume, i.e., a layer of only 10 nm over a spot of 5 μm, becomes a major bottleneck. Amongst the many experimental approaches attempted, we found the cryo-freezing and subsequent lyophilisation of aqueous solutions to be the most suitable [18]. The objective of this paper is to describe the methodological study for semi-quantitative characterisation of inorganic salt mixtures at the different levels of analytical complexity. As the sample preparation starts from solution, we have to use salts with a common anion or cation in this methodological study to avoid standards with ill-defined composition of the surface vs. bulk.

Specifically, three test cases will be described. First, the NaBr–KBr mixture is the most straightforward one by its structural simplicity. The second step involved mixing two different oxysalts, Na_2SO_4 and Na_3PO_4, in which case the fragmentation into oxides may introduce additional errors. Finally, we studied the Na_2SO_4–Na_2SO_3 system as an example of the most difficult case, involving so-called fine speciation, i.e., analysis of salts with the same elements in a different oxidation state. The complication is due to the fact that solid-state ionisation tends to cause oxidation or reduction of the original analyte, at least to some extent [19,20]. Hence, the presence of minor signals from sulphites in mass spectra from sulphates, and vice versa, can be expected to limit the capabilities of FT LMMS for semi-quantitative characterisation.

2. Experimental

2.1. Sample preparation

All the mixtures are prepared by fast freezing of a 10 μL aliquot of an aqueous solution, containing 10–20 g L^{-1} of analyte. Once the vacuum chamber is pumped to a pressure of 10^{-3} mbar, the sample holder is cooled with liquid nitrogen. The in-house developed set-up is described elsewhere [18]. After 30 min, the liquid nitrogen is replaced by a bath of melting ice for about 2 h. Subsequently, the sample holder-cooling unit reaches room temperature by exposure to air.

For the preparation of the mixtures commercial products (analytical grade) were used (Merck, Germany). Table 1 lists the mixtures made and the relative molar concentrations.

2.2. FT-LMMS measurements

The instrument [13] has been developed from a Spectrospin CMS 47X FTMS (Bruker Spectrospin, Billerica, MA, USA). The system uses an Infinity Cell™ [21], a 4.7 T magnet and an external ion source. Static electrical fields transport the ions from the source into the cell. In-house designed ion optics in the transfer line has improved the transmission by a factor of 10 [22]. The pressure in the cell and source are typically 4×10^{-10} and 10^{-8} mbar, respectively. The samples are irradiated at 45° in the reflection mode by a frequency-quadrupled Nd:YAG laser (Quanta–Ray DCR 2-10, Spectra Physics, Mountain View, CA, USA) at a wavelength of 266 nm. The beam spot on the sample is 5 μm. The typically used power density on the sample during irradiation is estimated to be 10^9–10^{10} W cm^{-2}. Due to the use of 8 ns laser pulses and the ion transfer with static electrical fields, the time between the laser pulse and the end of the ion injection in the cell (T_{gate}) determines the *m/z* range of the ions, which can be trapped simultaneously [13]. Practically speaking, for the *m/z* range considered in this paper, ions with *m/z* within 0.25 decade can be trapped simultaneously (e.g., *m/z* 100–250) on the condition that all ions are formed at the same moment, place in the selvedge and with the same initial velocity (direction and speed). The voltages used on the different electrodes (described in [22]) for positive ion detection are sample holder 0–3 V, shield +5 V, pusher 23 V; source housing −25 V; extractor 10 V, extractor lens −240 V; 1st flight tube −2215 V; 1st lens −900 V, 2nd lens −1000 V, 2nd flight tube −1500 V, 3rd lens −780 V, 3rd flight tube −1771 V. The cell plate voltages are at about 1 V. The cell introduction

Table 1
Survey of the mixtures studied, the characteristic ions to be used and the concentration range in mol%

Analyte		Ions used	Mol% of analyte I
I	II		
NaBr	KBr	$NaBr{\cdot}Na^+$, $NaBr{\cdot}K^+$, $KBr{\cdot}K^+$	30%, 50%, 75%, 90%
Na_2SO_4	Na_3PO_4	$Na_2SO_4{\cdot}Na^+$, $Na_3PO_4{\cdot}Na^+$	10%, 30%, 50%, 70%, 90%
Na_2SO_3	Na_2SO_4	$Na_2SO_3{\cdot}Na^+$, $Na_2SO_4{\cdot}Na^+$	0%, 10%, 30%, 50%, 70%, 90%, 100%

lenses are at − 3 and − 6 V and the acquisition time is about 0.5 s.

3. Results and discussion

The preparation of the reference mixtures is critical for the entire quantitative speciation. The optimised sample preparation is described elsewhere [18] and yields extremely small microcrystals arranged in sponge-like structures with a typical diameter of the filaments of about 0.5 μm. The depth-of-focus in our FT LMMS (2.5 μm) is sufficient to overcome the height difference. Particular attention has to be given to the absence of large crystals, which would indicate significant recrystallisation.

3.1. Binary salts

The electron volts photon interaction with the solid creates ions with significant structural specificity [1,17,19,20]. Basically, the mass spectral pattern consists of few intense peaks, due to the atomic ions in the low *m/z* range and the signals from ions that can be seen as their adducts of neutrals, most of which are the original analyte molecules. In some cases, e.g., oxysalts, oxides may act as neutrals as well and some cluster type ions (clusters are ions comprising of elements that were not originally neighbours in the sample) with low structural specificity occur in the low *m/z* range.

The simplicity and structural specificity of the mass spectra for speciation is related to the type of the ionisation processes [1,23]. Specifically, the laser microbeam irradiation is assumed to bring the neutral analyte (or ion pair) unchanged into relatively dense gas phase just above the original sample surface or "selvedge." Subsequently, the desorbed species are converted to charged adducts by uptake of a codesorbed atomic ion or small fragment ion. The experimental evidence for significant ion formation after the laser pulse supports this selvedge model as opposed to the direct ejection of the detected charged species from the solid [23].

Since alkali halides MX consist only of two elemental moieties, each of which only has one stable oxidation state, complications due to decomposition products or oxido-redox reactions do not occur. The base peak in the positive ion mass spectra is due to M^+, while the monomeric adducts $MX{\cdot}M^+$ are detected with a relative intensity of typically 50% [19]. The cationisation of two neutrals is seen but the corresponding signal shows a much lower abundance by typically a factor 5. In the negative ion mode, the atomic ions and monomeric adducts $MX{\cdot}X^-$ prevail, while the relative intensity of the dimeric adducts is much lower than for the positive ions. The yield of the positive vs. negative ions is higher for the cations. As to the mixture analysis, the monomeric adduct ions in the positive ion mode are the best choice to combine molecular specificity and sensitivity. The partial mass spectrum in Fig. 1 recorded from a NaBr–KBr standard containing 30 mol% NaBr shows the predominance of the signals due to $NaBr{\cdot}Na^+$, $NaBr{\cdot}K^+$ or $KBr{\cdot}Na^+$ and $KBr{\cdot}K^+$. According to the tentative model for DI [1,23], the adduct ions are related to the ion–molecule interactions between the laser generated neutrals (ion pairs) and the co-desorbed cations. It also implies that the combination of neutrals from Component A and ions of Component B (cross-contamination) must be accounted for properly when signal intensities are to be related to the local analyte concentration.

The local sample morphology (such as particle size and the way they are stacked on the substrate) determines the reflective and refractive properties of the locally irradiated spot. As a result, the initial energy deposition, its dissipation and the way it builds up an energy gradient at the surface from where the analyte ions are detected, can be slightly different from spot to spot. As a result, the total ion current (TIC) generated tends to show substantial shot-to-shot variations whereas the relative contributions of the individual ion species exhibit much smaller variations. Apparently, the shot-to-shot variability in TIC particularly applies in the low energy regime, which is used to generate molecule-specific analyte adducts. Quantification using atomic ions has been demonstrated for

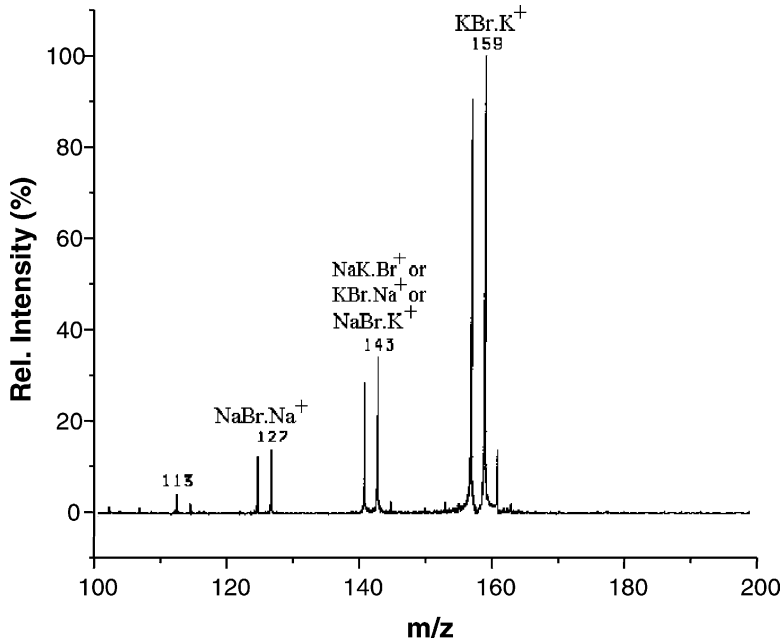


Fig. 1. Positive ion mass spectrum of a 30–70 mol% NaBr–KBr recorded by FT LMMS using a T_{gate} of 350 μs and laser power density of 9×10^9 W cm^{-2}.

alloys [9]. One of the possible ways to compensate for the fluctuations in absolute intensities is the use of an internal standard. Several approaches have been described for biomedical sections, e.g., a metal or dielectric coating applied by vacuum deposition in the vicinity of the analysed area, or ion implantation [24–26]. However, these approaches are unpractical for the analysis of as received solids and the normalisation on the TIC becomes a workable alternative. Due to the T_{gate} effect and the confined *m/z* window in FT LMMS, normalisation to the partial "TIC" means summing over few different *m/z*. Therefore, taking the ratios of the analyte specific signals becomes equally practical on the condition that the distribution of the TIC per analyte over all *m/z* remains constant from shot-to-shot.

As intensity ratios of specific peaks for the individual analytes are taken as concentration-dependent parameter, the reproducibility of relative intensities becomes a determining factor in the quantitative characterisation of mixtures. It comprises the contributions from the inherent instrumental errors, from the ionisation process and from the possible heterogeneity of the standards. The first contribution is assessed by isotope ratios, as laser ionisation at 266 nm is not isotope selective. The R.S.D. is within the 1–2% range. The value increases to 5% for peak intensity ratios of different adduct ions generated from one analyte. The experimental error on the intensity ratios of adducts from different analytes in mixture lies between 4 and 7%. In our opinion, the additional uncertainty introduced by sample preparation and/or ionisation of distinct species is considered as reasonable.

Fig. 2 shows the adduct ion intensity ratio $KBr{\cdot}Na^+/KBr{\cdot}K^+$ as a function of the analyte concentration. For the practical calibration it does not make a difference if the $NaKBr^+$ ion actually arises from the cationisation of KBr by Na^+ or from K^+ attachment to NaBr since both composing "entities" are coming from a different analyte. The calibration function typically takes the form of an exponential, which may look uncommon in analytical chemistry

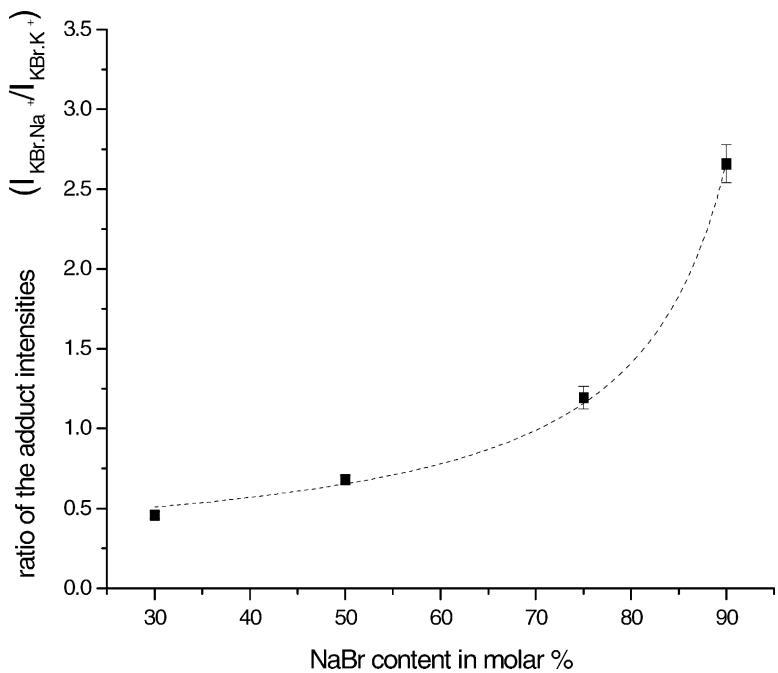


Fig. 2. Empirical calibration of the relative peak intensities of selected adducts ions as a function of the concentration in a NaBr–KBr mixture.

but has to be expected when the ratio of signals from major components is plotted as a function of the molar fraction. Assuming a perfectly "linear" dependence of the $NaBr{\cdot}K^+$ and $K{\cdot}KBr^+$ signal intensities on the local concentration of the respective salts, and thereby complete absence of matrix effects, their ratio should be given by:

$$I_{KBr{\cdot}Na^+} = k[\text{mol fraction KBr}][\text{mole fraction NaBr}] = k(1-x)(x)$$

$$I_{KBr{\cdot}K^+} = k'[\text{mol fraction KBr}][\text{mole fraction KBr}] = k'(1-x)(1-x)$$

where x = mole fraction of NaBr and $1-x$ = mole fraction of KBr.

This simple formula also shows that the way that NaKBr ions are described as cationised NaBr or KBr makes no difference to the final calibration function. The best fit for the response as a function of the local concentration is provided by: $y = 0.40+0.25x/(1-x)$ with y = peak intensity ratio of $KBr{\cdot}Na^+/KBr{\cdot}K^+$. Replicate measurements yield the same type of calibration curve but with slightly different values of both fitting parameters. It must be stressed that the calibration only aims at being empirical in nature. The concentration range for quantitative characterisation of this particular mixture goes from 30 to 90% and, in practice; the changes in the measure intensity ratio are small between 30 and 60%. This is inherently linked to the nature of the $x/(1-x)$ dependence of the ratios on x. Less expected is the apparent offset of 0.4, which is to some extent related to the limited dynamic range of FT LMMS [1]. Note indeed that the plot starts from 30% onwards. On the other hand, space charging effects readily disturb the analytical precision of peak ratios. As the KBr is the component with a higher ion yield than NaBr, the space charge effects are expected to reduce the peak intensity in the denominator of the adduct ratio for the low NaBr content of the mixture.

The uncertainty of the quantitative characterisation of a local mixture halfway the concentration range is about 3%.

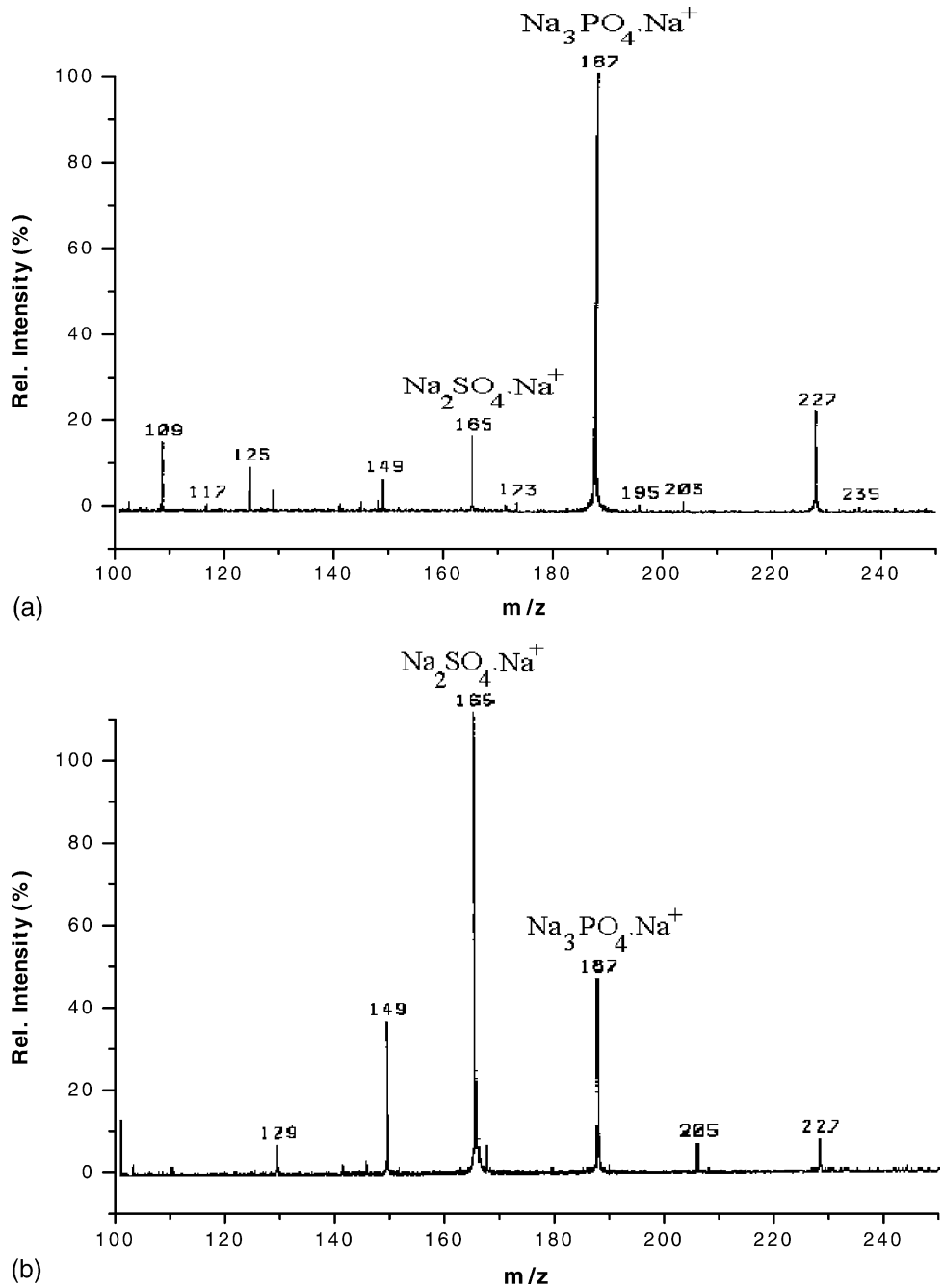


Fig. 3. Positive ion mass spectra of 10–90 mol% (a) and 90–10 mol% (b) mixtures of Na_2SO_4 and Na_3PO_4 using a T_{gate} of 350 μs and laser power density of 9×10^9 W cm^{-2}.

3.2. Oxysalts

The systematic studies on the speciation of these compounds have shown the additional complication due the partial decomposition of the original analyte into oxide species whereas sulphates produce also sulphite neutrals to be used in adducts [19,20]. The point to be addressed here is to what extent these reactions affect the use of the selected adducts ions for quantitative characterisation of the mixture. Again the positive ion detection mode provides higher yields in comparison to the negative mode for sulphates and phosphates molecular adducts. The ions used for quantitative characterisation are the cationised adducts of both analytes, i.e., $Na_2SO_4{\cdot}Na^+$ at $m/z = 165$ and $Na_3PO_4{\cdot}Na^+$ at $m/z = 187$. Fig. 3 shows the partial mass spectra at the optimised T_{gate} for two concentrations. The additionally seen signals at lower *m/z* refer to $Na_2S{\cdot}Na^+$ ($m/z = 101$), $NaPO_2{\cdot}Na^+$ ($m/z = 109$), $NaPO_3{\cdot}Na^+$ ($m/z = 125$) and $Na_2SO_3{\cdot}Na^+$ ($m/z = 149$). The first one is to be considered as a cluster ion because it reflects the combination of atoms from non-adjacent positions in the original sample. Also the $NaPO_2{\cdot}Na^+$ has low structural relevance in that there is no logical pathway for its formation. In contrast, as phosphoric acid is to be considered as the hydrate of orthophoshoric acid, $NaPO_3{\cdot}Na^+$ indeed carries structural information. The signals at $m/z = 205$ and $m/z = 227$ are to be assigned to the simple addition of the H_2O and NaOH as neutrals to the ions at $m/z = 187$.

Fig. 4 shows the calibration curve for the adduct ion intensity ratio $NaSO_4{\cdot}Na^+/Na_3PO_4{\cdot}Na^+$ in the concentration range of 10–90 mol% Na_2SO_4. The type of fitting function is similar as in the previous case $y = 0.19 + 0.24x/(1-x)$. Again the low slope in the first half of the concentration range considered hampers quantitative characterisation. The situation improves by the fast increasing adduct intensity ratios >50%. The R.S.D. is within 5% which allows the uncertainty on the local content determination to be estimated within 3% for a concentration around 50% Na_2SO_4.

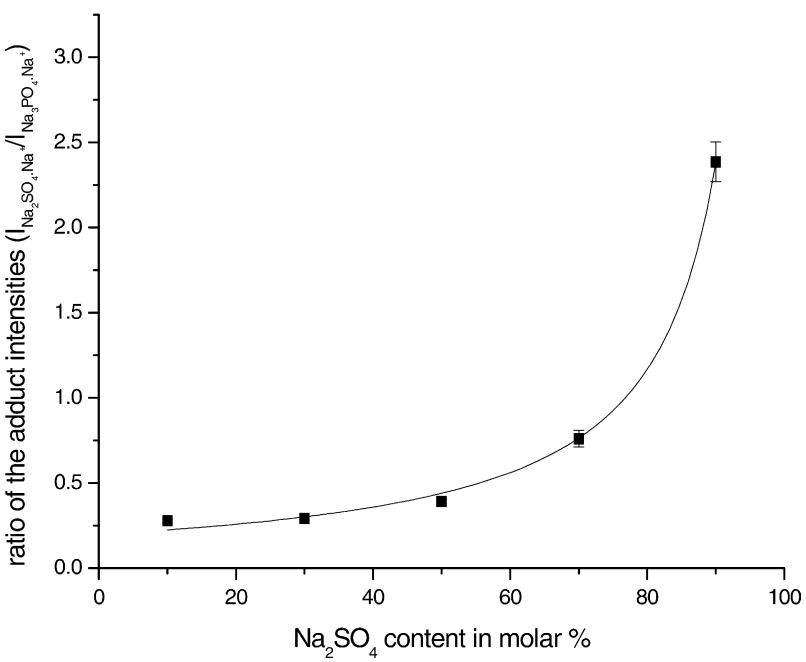


Fig. 4. Empirical calibration of the relative peak intensities of selected adducts ions as a function of the concentration in a Na_2SO_4–Na_3PO_4 mixture.

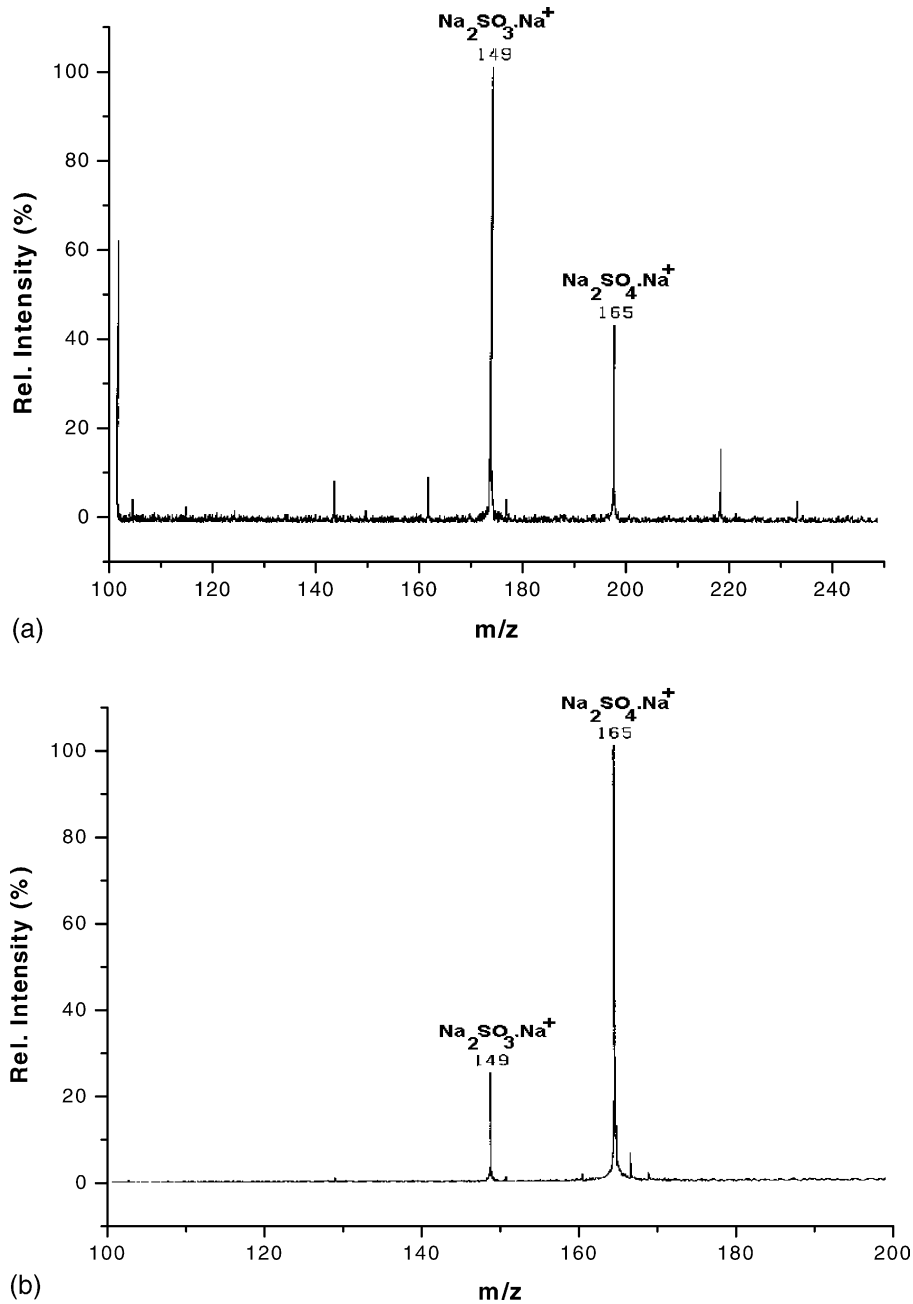
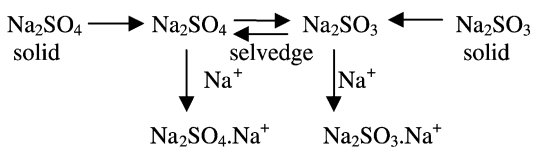


Fig. 5. Positive ion mass spectra of pure Na_2SO_3 (a) and Na_2SO_4 (b) recorded by FT LMMS with a T_{gate} of 350 μs and laser power density of 9×10^9 W cm^{-2}.

3.3. Fine speciation

The most complicated case occurs in the mixture analysis of two compounds with the same elements but in a different oxidation state, e.g., Na_2SO_3 and Na_2SO_4. Again, the relative intensities of the signals from $Na_2SO_4{\cdot}Na^+$ (cationised sulphate, $m/z = 165$) and $Na_2SO_3{\cdot}Na^+$ (cationised sulphites, $m/z = 149$) are the most useful to be considered for quantitative characterisation. However, the desorption–ionisation from solids by photon or kiloelectron volt-ion beams not only makes the intact analyte available in the selvedge for subsequent ionisation but also some oxidative-reductive processes take place before adduct ionisation occurs [19,20]. The latter cause sulphite adducts to be generated from sulphates and vice versa as shown in the following scheme:



Although the occurrence of the oxido-reductive processes hampers the molecular specificity of the detected ions, the cationisation of the form originally present in the sample yields more intense signals than the cationisation of the converted (oxidised or reduced) form. Fig. 5 shows that the peak intensity ratio $Na_2SO_3{\cdot}Na^+/Na_2SO_4{\cdot}Na^+$ is about 2 in the case of pure sulphate samples and about 0.3 in the case of pure sulphite samples. This effect inherently reduces the dynamic range for the intensity that can be used for quantitative characterisation. Note that this cross-contamination cannot be considered as a simple blank contribution to be subtracted from the signals. The diagnostic ions to be used ($m/z = 149$ and $m/z = 165$) in mixtures will originate in part from both analytes. Additionally, the importance of the oxido-reduction processes may vary depending on the presence of primarily sulphates (mixtures with low Na_2SO_3 molar content) or sulphites in the selvedge from mixtures (high molar content of Na_2SO_3).

Fig. 6 shows the experimental results for this system. The empirical best fit for the signal intensity

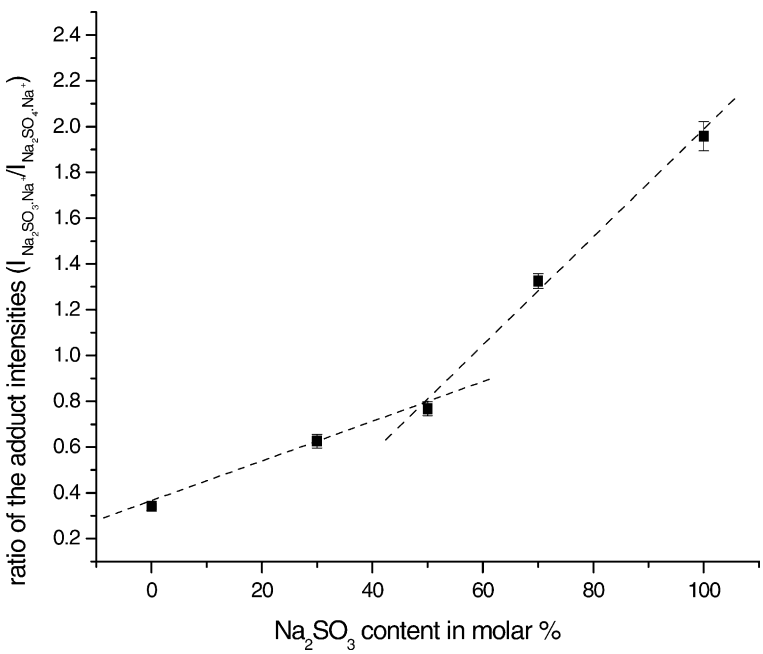


Fig. 6. Empirical calibration of the relative peak intensities of selected adducts ions as a function of the concentration in a Na_2SO_3–Na_2SO_4 mixture.

ratio of $Na_2SO_3{\cdot}Na^+/Na_2SO_4{\cdot}Na^+$ turns out to be a combination of two straight lines with an inflection point at the 50 mol% Na_2SO_3 mixture. The difference with the previous calibration curves can be seen as the result of some matrix effects, i.e., the ion yield of a given analyte depends on the relative abundance of the other component in the ionised microvolume. Specifically, the slope in the low and high Na_2SO_4 concentration range is tentatively associated with the changing importance of the oxido-reduction processes in the selvedge containing primarily sulphate and sulphites. It is readily conceived that the extent of the oxido-reduction may vary in a non-linear way with the selvedge composition. The ion yield of a given analyte depends on the relative abundance of the other component in the ionised microvolume. Therefore, the use of two lines with a different slope for the calibration of the signal intensities as a function of the local concentration is to be seen as a purely empirical way to elaborate a workable methodology for semi-quantitative assessment. This does not affect the point of major interest. Even in the "difficult" case of fine speciation mixtures, the uncertainty on the quantitative characterisation is to be estimated around 10 and 4% at 30 and 70 mol% Na_2SO_3, respectively.

4. Conclusion

For the first time it has been demonstrated that FT LMMS can be applied to the quantitative characterisation of inorganic binary mixtures by means of molecular adduct ion signals with a spot of 5 μm. The relative signal intensities are calibrated empirically as a function of the local content. The uncertainty on the derived concentration is between 3 and 10% which is in our opinion acceptable for a micro-analytical characterisation of solids on a microscopic scale with the high specificity of molecular information and high mass resolution. The calibration of the relative intensities for the diagnostic ions as a function of the local concentration reflects a linear dependence on the relative concentration of the individual analytes ($I_x/I_y \sim x/(100 - x)$) except in the case of fine speciation mixtures. A combination of two lines with a different slope for the low and high concentration range is found to be an empirical way to calibrate fine speciation mixtures. Consequently, the results have finally brought the uncertainty on the semi-quantitative characterisation of major components in local mixtures at the level of the precision achieved in the measurements of isotope ratios in LMMS. The feasibility of quantitative analysis has been a matter of debate for quite some time. Our experiments have shown that this largely relates to the preparation of suitable reference samples with homogeneous composition within the analysed microvolume. The use of the previously developed method of fast freezing and lyophilisation has been found to be successful to overcome the major bottleneck of standard preparation.

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