

Accurate calibration of on-line Time of Flight Mass Spectrometer (TOF-MS) for high molecular weight combustion product analysis

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Introduction

Time of flight mass spectrometry (TOF-MS) is a powerful analytical technique presenting the unique feature to allow identifying molecular weights of single species or mixtures and having information on their chemical functionalities in ranges from few Da up to hundreds of thousand of Da. However, accurate calibration by standard molecules in the same mass range of analytes is mandatory. Calibration in a very large molecular masses range is a stringent problem in studies focusing on detection of soot precursors from the polycyclic aromatic hydrocarbons (PAH) (namely, up to 300 Da), to high molecular weight species (large PAH, aromers, nanoparticles) extending till thousands of Da. However, in gas phase the only standards generally available are constituted by gas noble mixtures, therefore covering a small mass range for calibration, up to 136 Da (higher mass isotope of Xenon).

In literature, mass spectrometers (MS) calibration in larger mass ranges was reported by using water clusters especially for biological applications (e.g. for calibration in magnetic sector instruments [1], or quadrupole MS [2,3] up to near 1000 Da, and electrospray ionization MS up to 1900 Da [4]). It was found [5] that singly protonated water clusters are ideal calibration standards as they do not suffer from the complications of multiple charging (more than double charge), standard decomposition, memory effect or cation adduction, that can largely complicate the calibration process, as it occurs by using conventional reference compounds. However, in all this cases, both the calibrants and the analytes are injected into the MS source in liquid phase and the mass range was extended at maximum up to 1900 Da.

In the present work, for the first time to the best of our knowledge, accurate calibration of a Molecular Beam (MB) TOF-MS system is presented by using water clusters formed by condensation of water vapor in the supersonic beam as it passes from the atmospheric to low pressure region of the source through an orifice. This calibration has been applied to an (MB) TOF-MS recently developed and successfully applied to the on-line analysis of combustion products from atmospheric pressure combustion systems.

With this apparatus, water clusters up to 160 water molecules have been detected, therefore extending the calibration range up to more than 3000 Da, in the optimal operative conditions.

It was shown that in a MB-TOF MS apparatus for on-line detection of combustion products the water clusters for calibration can be formed from combustion water in particular operative conditions [5]. So that, water clusters can be used like superior calibration compounds as it is possible to calibrate the system for the analysis of combustion products before each set of measurements, without any necessity of changing the injection system for introducing external standard molecules.

A quantitative comparison with the traditional calibration by noble gas mixture in attributing the masses to a test mixture extending up to 800 Da is also reported, in order to show the advantage in using water cluster calibration for detection of analytes with masses much above noble gases. The implications of the increased mass accuracy and wider mass-to-charge ratio scale for the study of soot precursors are discussed.

Experimental

MB-TOFMS. All the experiments were performed using an apparatus based on Molecular Beam Time of Flight Mass Spectrometry (MB-TOF-MS), basically composed of: (i) a reservoir, (ii) a transfer line, (iii) a supersonic molecular beam, and (iv) a reflectron TOF-MS instrument (Kaesdorf s.r.l.), where different types of ionization sources can be used (e.g. electron impact ionization and multi-photon ionization with laser radiation). The TOF-MS system can be operated with a mass filter to deflect the lowest mass ions in order to preserve the dynamic range of the detector when signal intensities corresponding to low-mass ions are very high. More details on the TOF-MS system have been reported in a previous paper [5].

Samples. Water clusters are detected within the combustion product MB-TOF mass spectra when dilution and temperature are carefully chosen. In order to compare different calibration methods in this work water cluster were generated from a reservoir where distillate water was kept at a temperature of about 23°C in nitrogen atmosphere, while the carrier gas pressure is kept constant at 3 bar, which are found to be the optimal conditions for obtaining larger clusters. The nitrogen flow enriched with water was guided by a 3mm (i.d.) steel tube from the probe up to the vacuum chambers of the TOF-MS system.

When the calibration with noble gases was performed, a mixture of noble gases (5% Ar, 2% Kr, 5% Xe, balance He (mole percent)) at 5 bar pressure was used.

As test mixture for comparing noble gases and water clusters calibrations it has been chosen a mixture of water/ethanol (5% in weight of ethanol) that, in the system described above, produces water/ethanol and ethanol/ethanol clusters with molecular weights up to about 1000 Da.

Calibration. Calibration of the mass-to-charge ratio (m/z) (Da) scale of the mass

spectrometer is an important step in obtaining reliable mass spectra that typically involves analysing a calibration compound which yields ions of known m/z . The m/z scale is then adjusted to give the correct values for the calibration peaks.

In a TOF analyzer the following relation between the mass-to-charge ratio and the corresponding time of flight (t) (μs) holds [6]:

$$m/z = A + Bt + Ct^2 \quad (1)$$

The constants A, B and C depend on the electrical characteristics and geometry of the mass spectrometer.

Results and discussion

Water clusters are multimers of water molecules held together by extensive hydrogen bond networks [7]. They are formed by condensation of water vapor in the supersonic beam as it passes from the atmospheric to low pressure region of the source through an orifice [8].

A water cluster series spectrum from 50 to 1000 Da acquired with electron impact ionization is reported in Fig.1. The use of the mass filter to increase the sensitivity toward higher masses strongly reduces the signals below m/z 50 Da. For this reason in the following we report the mass spectra starting from this m/z value.

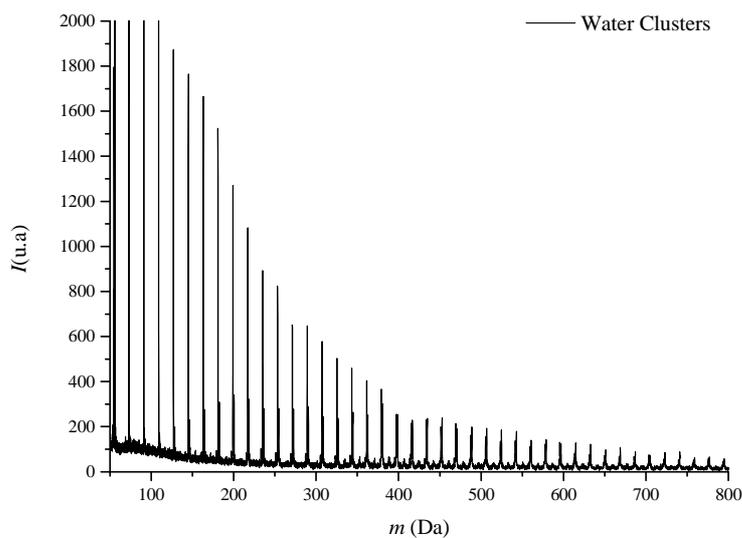


Figure 1. Water cluster series mass spectrum, acquired in reflectron mode.

Moreover, all the spectra here reported are acquired in reflectron mode, in order to have a better resolution (resolution around 1000, whereas in linear mode the resolution is 160). The resolution is calculated as the ratio of the mass of interest, m , to the lowest resolved difference in mass, Δm , as defined by the width of a peak at 50 % of the peak height: $m/\Delta m$ [6]. In linear mode, the increased sensitivity of the detector allows to extend the detection range up to 3000 Da (around 160 water molecules). The spectra here reported are all acquired with electron impact ionization, however we found similar results by using multiphoton ionization by a laser at 355 nm wavelength.

The water clusters appear to be ideal calibrant as they present a regular series of mono-protonated ions evenly spaced through the mass range and do not cause dirtying of the source. Moreover, metastable and double-charged peaks present in the spectrum over 400 Da are identifiable and do not generate confusion with the main peak sequence.

In order to test the performance in terms of mass accuracy and reduced error in mass attribution at high molecular weight ranges, two calibrations have been done by using alternatively gas noble mixture and water clusters. The resulting calibration constants together with their errors are reported in Table 1.

Table 1. Calibration parameters evaluated from the fit and their standard errors.

<i>Parameter</i>	<i>Noble Gas calibration</i>		<i>Water Cluster calibration</i>	
	<i>Value</i>	<i>Standard error</i>	<i>Value</i>	<i>Standard error</i>
C (Da)	-8.85038	0.5523	-0.2007	0.3091
B (Da·t ⁻¹)	1.4706	0.1193	-0.3202	0.03218
A (Da·t ⁻²)	0.8227	0.006110	0.9109	0.0007750

For quantitatively comparing the two calibrations procedures a test mixture, constituted by an ethanol/water solution, is introduced through the valve with nitrogen as carrier gas. Water clusters up to about 1000 Da are formed in the expansion into the molecular beam.

The formed clusters are constituted mainly by water/ethanol mixed clusters $[(C_2H_5)_m(H_2O)_nH^+]$ and both ethanol pure $[(C_2H_5)_m]$ and water pure clusters $[(H_2O)_nH^+]$ in dependence on the ethanol percentage in the solution.

After a preliminary identification of the peaks mass through a raw calibration, the exact mass of each peak has been evaluated (from nominal masses and raw formula identified) and reported in Fig. 2. In the same graph the calibration curves obtained by noble gases and water clusters calibration, have been reported.

It is evident the increase of accuracy calibrating by water clusters, that becomes more evident in the high masses range testifying the advantage in using these standards in particular for masses higher than 450 Da, where the accuracy of noble

gases calibration is about 3% whereas for water clusters calibration is lower than 0.1% (thirty fold reduction of mass error).

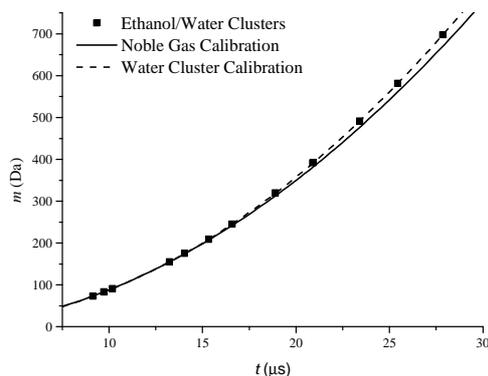


Figure 2. Comparison between the two calibration curves and the exact masses for ethanol/water clusters. Points represent the exact values of mass clusters.

In Fig. 3 the ethanol/water clusters spectra calibrated with the two standards are reported for comparison. As best visible in the inset reporting a zoom of the spectrum at high masses, it is noteworthy to observe that the shift between the peaks from the two spectra increases going toward higher masses.

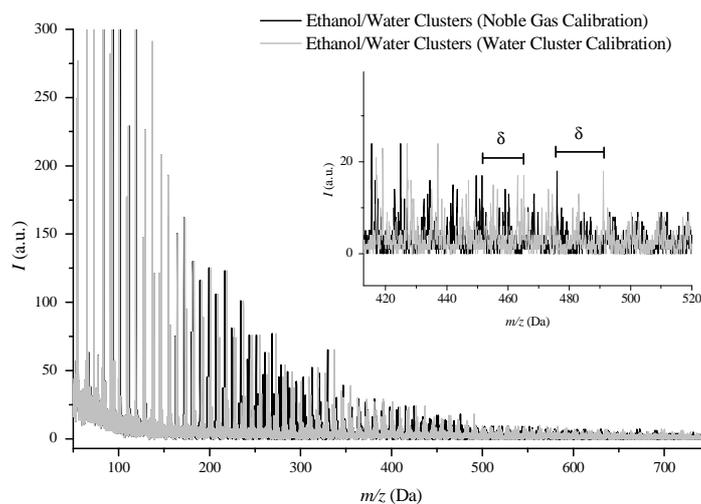


Figure 3. Ethanol/water clusters mass spectra, obtained using noble gas and water clusters calibration parameters in equation (1), reported in Table 1. In the inset of the figure it is also reported, for illustrative purposes, the shift (δ) between two peaks of the mass spectra.

The central issue in every mass spectral technique is the accuracy with which an analyte mass can be determined. The thirty fold reduction in mass error afforded by this method has heavy implications for application of MB-TOF-MS systems for soot mechanism study. Indeed, for masses just above the classical PAH (300 Da) a Δm of about 10 Da is present between the exact masses and masses measured by noble gases calibration, which means that, even if a high resolution instrument is employed, without a calibration in mass range so large to include the analytes masses, the accurate identification of single species or classes of species is hindered and therefore hypotheses on soot precursors structure and on soot inception mechanism lack validity.

A critical review on literature based on MB-TOF-MS detection of soot precursors should be done in light of the results reported in the present study.

References

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