

The ICP-ToF mass spectrometer: an alternative for elemental analysis

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Introduction

The velocity of an ion in an electric field is determined both by the power of the field and by the ion's charge-to-mass ratio. For ions having equal electrical charge, ions of lower mass will move faster than ions with higher mass. This property can be used to separate the ions according to their mass, whereby ions with increasing mass number hit the detector in a chronological order. This is the basic principle of operation for time of flight mass spectrometers (ToF-MS) used in analytical chemistry.¹

Although ICP-ToF instruments are not new, and have been commercially available for several years, we describe in this article a novel instrument built in our laboratory, which allows for a time resolution of 1 ns.² This instrument was developed to be capable of measuring complete mass spectra with high precision and sensitivity and high mass resolution, particularly from low sample amounts.²

Instrumentation

Figure 1 shows a schematic of a ToF mass spectrometer for elemental analysis. The sample to be analysed, normally as a solution, is introduced into a nebuliser, where a stream of argon gas breaks up the liquid into an aerosol. The small droplets are then swept into an inductively coupled plasma (ICP), which dries the droplets and causes the sample to dissociate and become partly ionised.

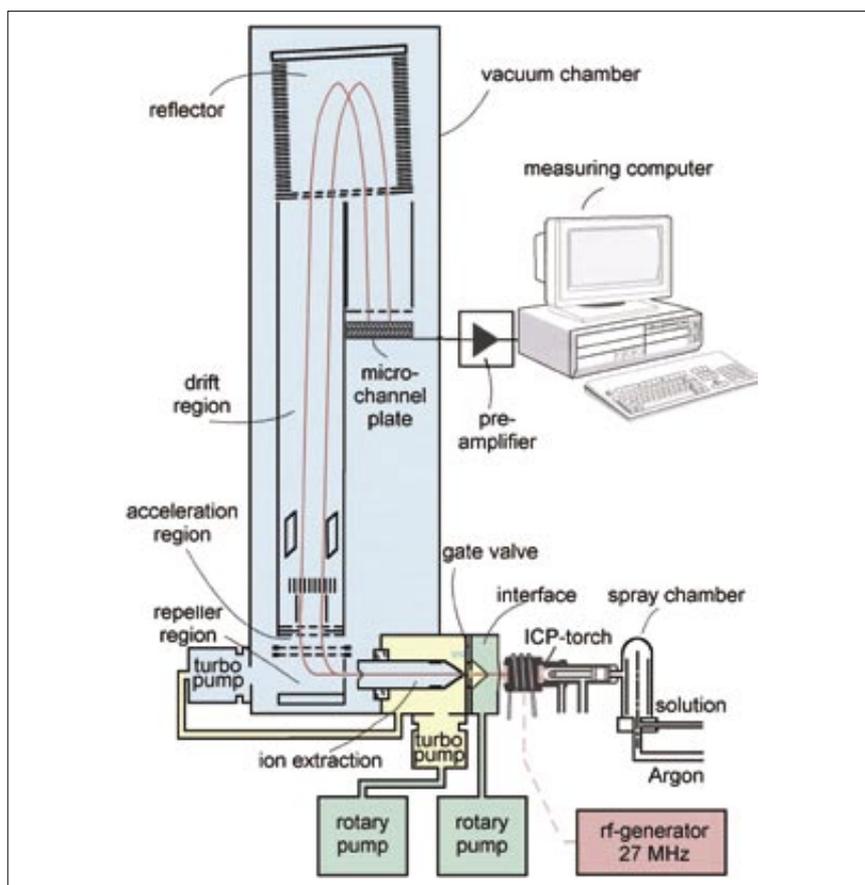


Figure 1. Schematic of a ToF mass spectrometer for elemental analysis.

A plasma stream containing the ions passes through the orifices of the sampler and the skimmer and enters a second vacuum chamber (at about 10^{-3} Torr) which is sealed tightly by a gate valve at the interface. Immediately following

the gate valve there is a second skimmer followed by an ion flight tube, both of which have a high negative potential (-2000 V) to extract the ions efficiently. Inside the ion flight tube a lens is inserted at a potential of -250 V. At the



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end of the ion flight tube there is a slit at a potential equal to that of the tube.

This system focuses the ion beam into the middle of the repeller region. To measure the ions' drift time a 2 μ s long voltage pulse of plus 800V deflects the ions into the direction perpendicular to the entrance direction of the repeller space. Then a voltage of –1870V accelerates the ions into the drift tube. Steering plates arranged perpendicularly to the axis of the drift tube direct the ion beam by electrical fields in the desired direction. Once in the drift region the ions move freely isolated from influence of any electric field.

Clearly the ion beam focused into the repeller space has a spatial extension across the entrance direction. Therefore, in the field of the repeller pulse, ions of equal mass experience a different acceleration depending on their start position. The smaller the distance of travel of the ions to the exit grid in the repeller space, the lower the velocity is of the ions passing the grid. However, these ions traveling a small distance to the grid gain a lead on ions covering a larger distance to the grid. After passing the acceleration space the faster ions make up the time gain of the slower ions in the drift tube free of influence from an electrical field. All ions of equal mass reach the same plane perpendicular to the drift tube axis (space focus) at a distance D from the acceleration grid at a certain time.

D does not depend on the ion mass but it essentially depends on the ratio of acceleration voltage to repeller voltage and on the height of the repeller space.³ D is about 20 cm for the ToF mass spectrometer of Figure 1. At this position an ion selector is located, which is used to remove unwelcome ions (⁴⁰Ar⁺ for example) from the drift path. The selector consists of a system of stainless steel slats in a parallel arrangement; each slat is 0.05 mm wide and 1 mm thick and they are positioned such that there is a 0.5 mm gap between them. The slats are contacted to the acceleration grid. If unwanted ions pass the slats a short positive pulse of about 200V is added. The shortest pulse duration that can be used is 30 ns. In this way single ion masses can be removed from the measured

mass spectrum. Ions of equal mass start from the drift tube space focus plane at the same time, however, with different velocities. Therefore with increasing flight time the mass separation of ions gets increasingly worse. To bring together ions of equal mass on the detector surface, ions are retarded by an electrical counter field and are reflected into a second drift tube. Fast ions need more time for this process than slower ions. In this way the time gain caused by higher velocity can be compensated for (velocity focus). The distance between the primary drift tube space focus plane and the velocity focus (detector surface) reduced by the length of the reflector is called the focus length L . For the mass spectrometer in Figure 1, L is about 60 cm long; the length depends essentially on the ratio of acceleration voltage to repeller voltage and on the length of the reflector.³

ICP-ToF mass spectrometry, a simultaneous technique

Most ICP quadrupole mass spectrometers used in elemental analysis today use quadrupole fields to effect the mass separation. Ions introduced in the space between the four quadrupole rods are caused to fluctuate by an oscillating electrical field. Conditions can be chosen such that only one ion mass has a stable pathway. All other ions leave the quadrupole before they reach the detector. Therefore the element determination is done successively one ion after another. A minimum time of 5 to 10 ms is necessary for the determination of each mass.

Because the ions of different elements measured by the detector are extracted from the plasma in temporal succession, the analysis technique is called sequential. A disadvantage of the sequential technique is the decrease of the correlation factor between measurement signals of the elements. Higher stability of the ion source (ICP) is necessary to compensate for this drawback.

A second disadvantage occurs if samples of limited amount need to be analysed, which results in transient measurement signals, such as occur in laser ablation.² The number of elements and their ions that can be measured is

limited fundamentally and depends on the duration of sample supply. In ToF mass spectrometers ions of all element ions arrive simultaneously into the repeller space and are deflected subsequently by the repeller pulse. The counting of ions of different elements by the detector proceeds in a temporal succession similar to that in a quadrupole mass spectrometer, but the ions from all elements originate from the plasma at the same point of time. Therefore, in contrast to the quadrupole mass spectrometer, the ToF mass spectrometer is a simultaneous technique. The signals of ions are well correlated with each other. To obtain high ion count rates it is necessary to avoid loss of ions in the repeller space. This will occur if the required filling time equals the time delay between two consecutive repeller pulses diminished by the pulse duration. By knowing the velocity of ions in the repeller space, the optimal repeller pulse frequency can be determined.³ Practically, the velocity of ions in the repeller space is equal to the velocity of the plasma beam leaving the interface skimmer.

For the ToF mass spectrometer of Figure 1 the optimal pulse frequency has been determined as 25 kHz so that the shortest possible analysis time is 40 μ s. In this time the instrument records essentially the full ion spectrum. In a ToF mass spectrometer, transient analyte signals can be measured with high time resolution and without any limitation in the number of elements detected as a consequence of only being able to introduce small sample amounts (μ L range) of sample into the ICP.

Instrumental figures of merit

The separation of ions that have different mass is characterised by the mass resolution A . A is defined by the ratio $A = m/\Delta m$ (1), where m is the ion mass number and Δm is the mass difference resulting from the temporal half-width ΔT of the measurement signal for the mass m . If the mass m is expressed in units of flight time then A is equal to $0.5T/\Delta T$. The minimum signal width ΔT_0 given by the ion detection system limits the resolution. In this case the resolution is

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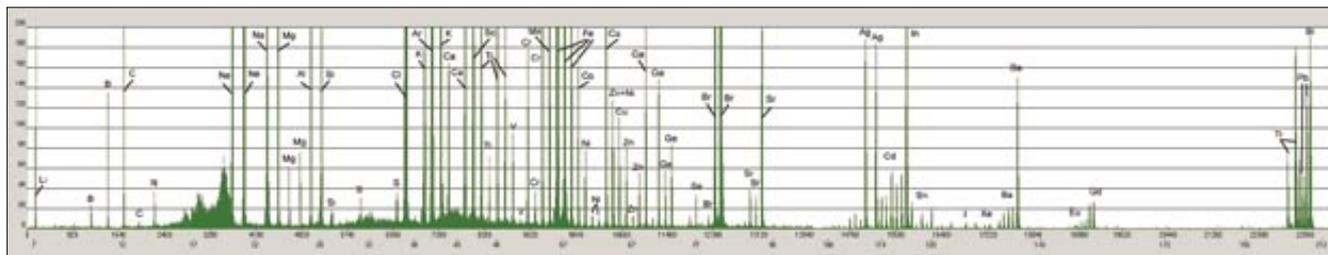


Figure 2. ICP-ToF mass spectrum recorded from $1 \mu\text{g L}^{-1}$ of a multi-element solution, 5 s measuring time, 125,000 sweeps.

$A=0.5T/\Delta T_0$; T and ΔT_0 are measured in ns.³

A multi-channel plate such as that used in the ToF mass spectrometer (see Figure 1) produces a pulse half width of 0.7–1 ns. To prevent an increase of the pulse width by subsequent signal processing, an ion counting technique was developed with super fast electronics for signal acquisition and dead-time free storing.

The main component of this fast signal counting electronics is an application-specific integrated chip (ASIC) working in the following manner: every pulse produced by an ion arriving at the detector must pass a test for real signal pulse identification, then the signal is carried forward into a 32-bit shift register, and if the register is filled the content will then be carried forward into internal storage. The cycle time is coordinated in such a way that during the time taken for storage a second shift register is filled alternatively. There is no dead time between signal identification and internal signal storage. The program takes 1 ns for one pulse. The pulse width of the detector determines the time resolution. ΔT_0 is 1 ns.³ Therefore, the theoretical maximum of resolution for lead isotopes is about 11,000 and for magnesium isotopes it is about 3800.³ Obviously in practice such resolutions are not achievable.

255 full spectra can be stored in the internal store. The accumulated spectra from the internal store are transferred via a fast bus system to a store of the operating computer for further calculations. Figure 2 shows the complete ICP-ToF mass spectrum recorded from a multi-element solution.

The space distribution of the ions in the repeller space causes an increase of the signal width with a concomitant

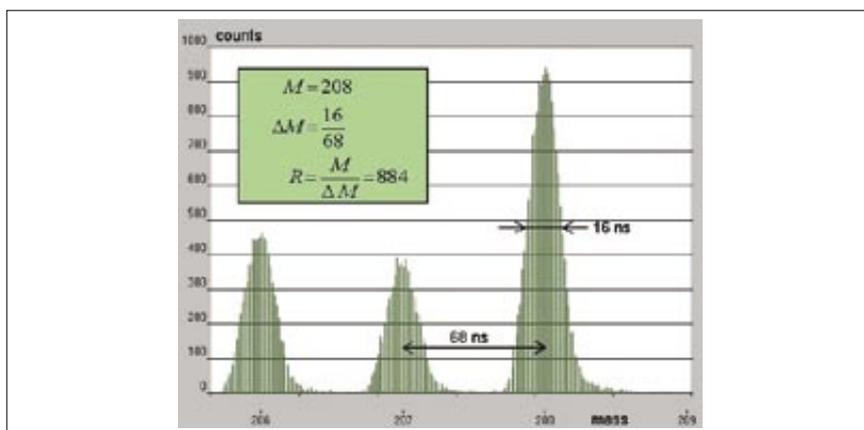


Figure 3. ICP-ToF mass spectrum example for the resolution of lead isotopes.

decrease in the resolution. If $\Delta\alpha$ is the ratio of the beam to the height of the repeller space, then A is proportional to $\Delta\alpha^{-2}$ ($A \sim \Delta\alpha^{-2}$). The factor of proportionality is higher than 1, equal for all ion masses and depends only on the ratio of acceleration voltage to repeller voltage.³ Changing the width of the slit in the ion flight tube can influence $\Delta\alpha$. At a slit width of 0.2 mm the resolution is about 600. Figure 3 gives an example for the resolution of lead isotopes.

A second cause for the signal broadening is the velocity component of the ions from the plasma that is perpendicular to the beam direction. The thermal velocity should be negligible because it corresponds to an equivalent of around $\Delta\alpha=0.001$ and therefore does not influence the resolution. A different consideration occurs when discharge processes caused by the bias potential of the plasma determine the ion velocity in the plasma. Consequently, the bias potential, which is produced by different velocities of the plasma electrons and ions in the RF field, should be as small as possible.

For this reason the plasma is grounded to the earth potential. In the ICP of Figure 1 this is carried out by a metal shield lying between the induction coil and the torch, which will be grounded after the plasma is ignited.

In addition to the resolution A , the performance of an ICP mass spectrometer is characterised by the ion extraction rate E . E is the measure for the number of those ions extracted from the plasma in a certain time interval and detected in the mass spectrometer.

For the ICP quadrupole mass spectrometer, E depends on the number n of the measured ions of elements. It will halve if n is doubled.³ In contrast, for the ToF mass spectrometer, E is independent

Table 1. Measured extraction rates.

MHz / ppm	
^{209}Bi , ^{208}Pb , ^{205}Tl , ^{115}In , ^{88}Sr , ^{57}Fe , ^{138}Ba , ^{59}Co , ^{23}Na	>10
^{107}Ag , ^{69}Ga , ^{63}Cu , ^{55}Mn , ^{52}Cr , ^{24}Mg	5–10
^{114}Cd , ^{64}Zn , ^{60}Ni , ^{27}Al , ^{11}B , ^7Li	1–5



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Table 2. Measured limits of detection according to the 3σ -criterion.

ngL ⁻¹	
²⁰⁹ Bi, ²⁰⁸ Pb, ²⁰⁵ Tl, ¹¹⁵ In, ⁸⁸ Sr, ⁵⁷ Fe	<1
¹³⁸ Ba, ⁵⁹ Co, ²³ Na, ¹⁰⁷ Ag, ⁶⁹ Ga, ⁶³ Cu, ⁵⁵ Mn, ⁵² Cr, ²⁴ Mg	1–5
¹¹⁴ Cd, ⁶⁴ Zn, ⁶⁰ Ni, ²⁷ Al, ¹¹ B, ⁷ Li	5–10

of n because all isotopes are measured simultaneously.

Obviously a loss of ions takes place on the grids through which the ion beam passes. In the ICP-ToF mass spectrometer depicted in Figure 1 *E* will be diminished by a factor of 0.3 if nine grids are installed

with a transparency of 88%. Table 1 gives a survey of measured extraction rates expressed in Hz, i.e. the number of ions measured per second, for a solution concentration of 1 $\mu\text{g mL}^{-1}$.

Analytical figures of merit

The spectral background and the sensitivity for a significant difference between analyte signal and background signal determine the performance of an analytical technique in the detection of elements. The measure is the limit of detection of an element that is given if the analyte signal exceeds the three-fold variance (3σ -criterion) of the background noise. Table 2 lists some examples for measured limits of detection.

A second analytical criterion is the dynamic range. It determines over what range of element concentrations

it makes sense to measure analytical signals. Basically the detector determines the dynamic range. In ICP-ToF mass spectrometry the well-defined signal measurement becomes limited in the counting mode when the temporal succession of ions hitting the detector is so short that double pulses occur. Therefore, the dynamic range of the detector is not exploited in the ICP-ToF mass spectrometer; as indicated in Figure 1, an additional analogue signal acquisition system is installed. The ion signals of the detector are simultaneously collected as in the counting mode, but processed by a fast AD-converter (10 ns) in the operating computer. This analogue mode is considerably less sensitive compared with the counting mode but permits an extension of the dynamic range of the analytical signals by about two orders of magnitude. Figure 4 shows an example.

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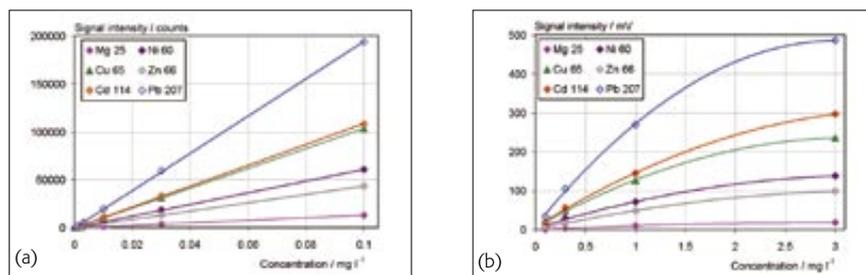


Figure 4. Dynamic range: (a) count mode, (b) analogue mode.

Summary

The ICP-ToF mass spectrometer described here is an excellent instrument for the analysis of small sample amounts—either liquid or solid—because of its simultaneous signal acquisition. In this area its performance exceeds all other techniques used at this time, in limit of detection, reproducibility and element

range. The ICP-ToF mass spectrometer is not merely an instrument that benefits laser evaporation and thermal evaporation sample introductions,² the ICP-ToF mass spectrometer is also an alternative for the sequentially measurement techniques of solution analysis. In many cases for instance in medical science or life science only small amounts of

sample are available. With the ICP-ToF mass spectrometer such samples can be analysed directly without any limitation on number of elements and any additional dilution step.

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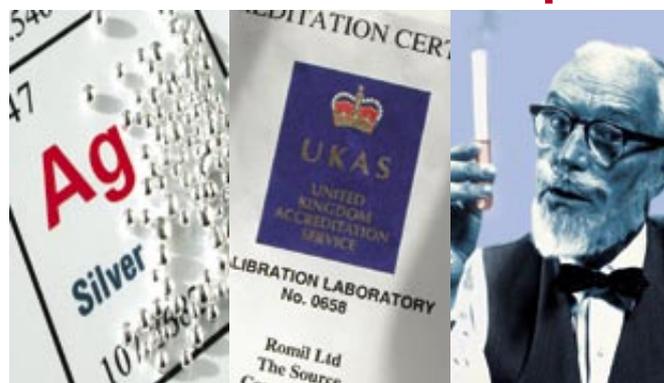
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