Characterisation of Nuclear Fuel Samples by Quadrupole and Multicollector Inductively Coupled Plasma Mass Spectrometry

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The characterisation of nuclear fuel cycle materials for trace and minor metallic constituents is of great interest for the nuclear industry and safeguard officials. The main objective of various international programmes dealing with post-irradiation examinations is to improve the knowledge of the inventories of actinides, fission and spallation products in spent nuclear fuels.

The low detection limits for a large number of elements combined with the ability to analyse the isotopic composition of the elements have established inductively coupled plasma mass spectrometry (ICP-MS) as a powerful multi-element technique in diverse analytical applications for the characterisation of nuclear materials. Because numerous isobaric overlaps restrict the direct determination of many fission products by mass spectrometry, extensive chemical separations are required for these elements. In order to simplify this sample preparation procedure, a high performance liquid chromatography system (HPLC) was online coupled to the mass spectrometer.

Since about 10 years a quadrupole based ICP-MS (Q-ICP-MS) combined with an HPLC is used within the Hot Laboratory of the Paul Scherrer Institut for different applications on nuclear fuel samples.

Since May 2003 also a new multicollector ICP-MS (MC-ICP-MS) is used for the mass spectrometric characterisation of nuclear fuel samples, especially for the precise determination of the isotopic vectors of fission products and actinides. Therefore, two complementary analytical systems are now available in the group of "Isotope and Wet Analytical Chemistry".

A comparison of the analytical performance of both systems (with and without an online coupled HPLC system) for the determination of the isotopic composition and the elemental concentration of different nuclides in nuclear fuel samples, the advantages and limitations of both techniques, the accuracy and precision of the results and typical applications for both methods will be discussed in the presentation.

KEYWORDS: nuclear fuels, HPLC, ICP-MS, isotopic dilution analysis, isotopic vectors

1   Introduction

The characterisation of nuclear fuel cycle materials for actinides, fission and activation products is of great interest for the nuclear industry and safeguard officials. The main objective of various international programmes dealing with post-irradiation examinations is to improve the knowledge of the inventories of actinides, fission and spallation products in spent nuclear fuels. The prediction of the source term of the mentioned nuclides is of greatest interest in numerous nuclear areas, such as:

- prediction of the fuel isotopic composition at different steps of the irradiation cycle and at the end of life for the definition of basic licensing data for UO_2 and MOX fuels
- the currently discussed increase of fuel enrichment may require a re-evaluation of criticality licences for transportation, storage and reprocessing of spent nuclear fuel based on burnup credit
- fundamental research programmes on actinides

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- necessity to improve the calibration of source term codes for high burnup and for MOX fuel recycling scenario
- safeguard issues

To fulfil all the listed objectives it makes sense to choose a wide range of different samples: Irradiated UO_2 and MOX fuel samples from both reactor types (PWR and BWR) and with various values for the burnup.

The low detection limits for a large number of elements combined with the ability to analyse the isotopic composition of the elements have established inductively coupled plasma mass spectrometry (ICP-MS) as a powerful multi-element technique in diverse analytical applications for the characterisation of nuclear materials. The quantification is normally carried out by isotopic dilution, which is known as the most precise quantification method for mass spectrometric analysis.

Numerous isobaric overlaps (e.g. $^{238}U/^{238}Pu$, $^{241}Pu/^{241}Am$, $^{147}Pm/^{147}Sm$, $^{148}Sm/^{148}Nd$ and $^{150}Nd/^{150}Sm$) restrict the direct determination of most actinides and fission products by mass spectrometry. Therefore, conventional methods for determining actinides and fission products in irradiated fuel samples require careful and mostly time-consuming separation steps of the analytes, followed by an off-line determination of the isotopic vector by e.g. thermal ion mass spectrometry (TIMS). The combination of the separation by high-performance liquid chromatography (HPLC) with the online detection by an ICP-MS allows the determination of isotopic vectors in one analytical step. This hyphenated technique was extensively used in the Hot Laboratory of the Paul Scherrer Institut (PSI) during the last years for the determination of isotopic vectors of actinide and fission product in irradiated UO_2 and MOX fuel samples.

Since about 10 years a quadrupole based ICP-MS (Q-ICP-MS) is used within the Hot Laboratory of the Paul Scherrer Institute for different applications on nuclear fuel samples (burnup analysis, characterisation of fresh fuel samples, determination of the isotopic vectors of fission products and actinides).

Since May 2003 also a new multicollector ICP-MS (MC-ICP-MS) is used for the mass spectrometric characterisation of nuclear fuel samples, especially for the precise determination of the isotopic vectors of fission products and actinides. Therefore, two complementary analytical systems are now available in the group of "Isotope and Wet Analytical Chemistry".

A comparison of the analytical performance of both systems (with and without an online coupled HPLC system) for the determination of the isotopic composition and the elemental concentration of different nuclides in nuclear fuel samples, the advantages and limitations of both techniques, the accuracy and precision of the results and typical applications for both methods will be discussed in the paper.

2 Experimental

2.1 Sample pre-treatment

After the arrival of the fuel pins at the Hot Laboratory in PSI the non-destructive post irradiation experiments (PIE) are accomplished, mainly:
- visual inspection of the fuel pin (damages, fissures)
- rod overall length and profilometry
- axial gamma scanning of the whole pin
- Eddy current oxide measurement
- fission gas release

After all these measurements the samples for the chemical analyses are defined, cut and transported into the shielded dissolution cell.

2.2 Sample dissolution

For some research programmes it is important to know the amount of ^{129}I and other volatile fission products. Therefore, at PSI two different dissolution procedures exist.

2.2.1 Dissolution of irradiated fuel <u>without</u> iodine capturing

For this type of sample dissolution a high pressure digestion bomb with a 250 ml PTFE inset is used. The irradiated MOX and UO_2 fuel samples from light water reactors (8 to 10 g) are dissolved in 20 ml of a 1:1 mixture by volume of HNO_3/H_2O (Merck, Suprapur). The equipment is heated for one hour at 150 °C. This step dissolves about 98 % of the sample. After cooling down the cladding is taken out of the system. Afterwards the metallic residues are dissolved in 25 ml of a 9:1 mixture by volume of HCl/HNO_3 (Merck, Suprapur) by heating four hours at 170 °C. The stock solution is diluted with 1 M HNO_3 to a concentration of 0.5 mg fuel per gram of solution.

2.2.2 Dissolution of irradiated fuel <u>with</u> iodine capturing

The dissolution procedure with capturing of volatile components – mainly iodine – is a two stage process. In the first step the irradiated fuel specimen is heated under reflux and the volatile components (mainly iodine) are captured. Afterwards the fuel solution is filtered. The filter cake with the residues is dried and dissolved in a second dissolution step.

The apparatus for the dissolution of the radioactive specimens consists of a round-bottom two-neck flask which is equipped with a reflux condenser and a separatory funnel. The flask is heated with help of a temperature controlled electrical heating mantle. A small vacuum pump sucks the escaping gases through three gas-washing bottles and an absolute filter. The first two bottles are filled with 30 ml of a 4 M NaOH solution and the released iodine is captured according to the following equation:

$$3\ I_2 + 6\ OH^- \leftrightarrow IO_3^- + 5\ I^- + 3\ H_2O$$

The third bottle is empty and protects filter and pump from NaOH solution. The water lock at left allows a visual adjustment of the gas stream and prevents an iodine gas stream in the wrong direction.

After having weighed the irradiated rod piece (normally containing three pellet gaps) the specimen is treated with hot 8 M HNO_3 in the round-bottom two-neck flask. Carrier iodine (^{127}I) has to be added before heating is started. After one hour at 130 °C a second portion of carrier iodine is added through the separator funnel. Then the flask is heated one hour at 150 °C and additionally four hours at 170 °C. Afterwards, the apparatus cools down during the night. The mentioned temperatures are measured in the electrical heat mantle and <u>not</u> in the dissolver solution. Adding the carrier iodine allows to determine the yield of iodine capturing.

After the first dissolution step the empty cladding and the slightly soluble residues have to be separated. Whereas the cladding can be removed mechanically the residual material has to be separated by filtration. LCR membrane filter made of hydrophilised PTFE with a pore size of 0.5 μm (Millipore FHLC 047 00) are used.

15 - 20 mg of the slightly soluble fuel components (residues) are dissolved in 20 ml of a mixture of 9 parts (volume) hydrochloric acid and 1 part nitric acid (Merck, Suprapur) in a high pressure dissolution bomb for four hours at 180 °C.

The dissolved residues are diluted with 1 M HNO_3 to 0.1 mg of the slightly soluble material per gram of solution.

2.3 Sample preparation

For isotope dilution analysis aliquots of the mother solutions were mixed with enriched isotopic spike standards and diluted with 1 % HNO_3. A further set of aliquots was directly diluted with 1 % HNO_3 without spike addition.

Aliquots of the spiked and unspiked sample solutions were injected three to five times into the HPLC-ICP-MS (quadrupole or multicollector) systems for the determination of the isotopic composition of the different elements.

2.4 Correction of Mass Bias Effects

Mass discrimination represents a limitation to the accuracy of isotope ratio measurements in all mass spectrometric methods. Ions entering the ICP-MS experience so called mass bias effects, and this bias favours the transmission of the heavier isotope into the mass spectrometer. In order to correct for these effects standard materials with a known isotopic

composition were analyzed together with the samples. The correction factor for the mass discrimination effects is calculated based on the ratio between the certified isotopic composition of the standards and the measured values using an exponential correction equation.

2.5 Instrumentation

2.5.1 HPLC

A DX300 HPLC system (Dionex, Switzerland) equipped with an IonPac CG5 or CG10 (4 mm x 50 mm) as guard and IonPac CS5 or CS10 (4 mm x 250 mm) as analytical column was used in combination with the Q-ICP-MS. The flow rate of this HPLC is 1 ml/min and the injection valve is equipped with a 1 ml sample loop.

For online coupling to the MC-ICP-MS a modern DX-600 GS50 HPLC system (Dionex, Switzerland) equipped with a CG5A (2 mm x 50 mm) as guard and a CS5A (2 mm x 250 mm) as analytical column was installed. Because of the smaller column dimensions the flow rate of this system is restricted to 0.25 ml/min and the injection valve has a sample loop of only 0.025 ml.[1]

The chromatographic separations were performed according to the methods described earlier[2].

The coupling of the HPLC systems to the corresponding ICP-MS is achieved by passing the effluent of the chromatographic column to a 4-way valve. All sample components separated on the chromatographic column can be either sent directly to the ICP-MS for analysis or to waste in order to keep the sample loading into the mass spectrometer to a minimum.

2.5.2 ICP-MS

Inductively coupled plasmas are used since more than 25 years as excitation source for the optical emission spectrometry. The possibility to analyse the ions that are produced in an argon plasma by a mass spectrometric detector was first described in the eighties[3].

In a **Q-ICP-MS** the ions entering the mass spectrometer are separated according to their mass-to-charge ratio in a quadrupole mass filter and the detection of the ions is carried out with an electron multiplier in a fast but **sequential** mode. Since the entire mass range can be measured with a Q-ICP-MS in less than one second, these instruments are suitable for multielemental analyses. However, the precision of isotope ratio measurements is not comparable to the classical TIMS technique, because of the sequential detection mode.

In a **MC-ICP-MS** the ions are normally separated in a magnetic sector field and the detection is carried out by a set of 9 to 12 Faraday cups that allow the **simultaneous** detection of different isotopes over a restricted mass range of about 15 %. Therefore, isotope ratio measurements of MC-ICP-MS can provide external precision as low as 0.002 % RSD for different elements[4-5]. These results are in the range of or even superior to TIMS, which has been the preferred method so far for highly precise isotope ratio measurements for elements with relatively low first ionization potentials, such as U, Pu and Nd.

The Hot Laboratory of the PSI is equipped with a PQ2+ Q-ICP-MS (ThermoElemental, UK) and a Neptune MC-ICP-MS (ThermoElectron, Germany) with nine Faraday cups.

For handling and analyzing highly toxic radioactive nuclear fuel samples parts of the respective HPLC system as well as the sample introduction part of the ICP mass spectrometers are encapsulated within glove-boxes.

3 Results and Discussion

3.1 Elements analysed by ICP-MS

For some of the nuclides which are of interest in an extensive characterisation of irradiated nuclear fuel no chromatographic separation is needed because no isobaric overlaps occur.

The concentration of the isotopes ^{237}Np, ^{95}Mo, ^{99}Tc, ^{101}Ru, ^{103}Rh, and ^{109}Ag was analysed by ICP-MS using the external calibration method with an internal standard. The sensitivity of the

instrument is determined for all of the isotopes by measuring different concentrations of calibration standards (at least 5 different concentrations of the standard and a blank solution). The calibration curve (concentration vs. intensity) is calculated based on a linear regression.

In order to correct for time-dependent signal instabilities and for the influence of different matrix concentrations in the sample an internal standard was used for all quantitative determinations by external calibration. The internal standard has to be added to all calibration standards, blank solutions and samples in the same concentration. As the internal standard an element must be chosen which is not present in the analysed samples and has a similar mass-to-charge-ratio as the elements to be determined. Common elements used as internal standards are e.g. Be, Sc, Y, In, Rh, Bi, and Th.

Where possible the quality of the ICP-MS measurements was controlled by determining the recovery rate of additional standard materials (see table 1).

Table 1:   ICP-MS measurements using the external calibration method with an internal standard. For the calibration curve a blank and at least 5 different concentrations of calibration standard were measured. Measuring mode: peak jumping with 1 point per peak and 10 s measurement time per repeat.

Nuclide	Internal Standard		No. of repeats	Recovery rate	Chemical form of the control standard
	Element	ng/g sol.		% (± 1 s)	
^{237}Np	Bi	50	10	99.1 ± 0.8	NpO_2
^{95}Mo	In	50	15	98.4 ± 2.3	MoO_3
^{99}Tc	In	50	10	[1]	
^{101}Ru	In	50	15	97.5 ± 1.5	Ru standard solution
^{103}Rh	In	10	10	[1]	
^{109}Ag	In	50	15	99.2 ± 1.2	$AgNO_3$

[1]   No control standard material available, neither in solid or dissolved form

The accuracy of the determined recovery rates are in the order of the accuracy of our quadrupole instrument for quantitative analysis.

3.2   Elements analysed by HPLC-ICP-MS

Due to isobaric overlaps some of the elements (e.g. Sr, Cs, Nd, Pm, Sm, Eu, Gd, U, Pu, Am, Cm) of an extensive characterisation of irradiated nuclear fuel have to be analysed with the hyphenated HPLC-ICP-MS technique.

All of the elements analysed by the on-line coupled HPLC-ICP-MS system (except ^{147}Pm) were quantified using isotopic dilution analysis (IDA). In principal, IDA is restricted to elements with at least two isotopes free of isobaric interferences. Because lots of these interferences occur in an unknown extent in fuel samples, all of the elements were separated with the chromatographic system. Since ^{147}Pm is mono-isotopic, a quantification using isotopic dilution is not possible for this element. Nevertheless, a chromatographic separation is also necessary because ^{147}Pm is interfered by ^{147}Sm. The quantification of ^{147}Pm was carried out by external calibration in combination with the HPLC separation.

For IDA a highly enriched isotopic spike is added to the sample solution ("spiked" sample). Additionally, an "unspiked" sample is analysed by HPLC-ICP-MS for its isotopic composition.

The elemental concentration in the fuel samples can be calculated based on the measured isotopic composition of the spiked and the unspiked sample, the certified isotopic composition of the spike itself and the known amount of the sample and the added spike. The highest precision of the data is achieved when the ratio between the measured isotopes in the spiked sample is near unity.

Because all dilution steps of the fuel stock solutions are carried out with 1 % HNO_3 (Suprapur), this solution is measured as "blank" between the standards and samples. These measurements are necessary in order to detect possible memory effects in the chromatographic system between the standard, the unspiked and the spiked samples. Memory effects would lead to a misinterpretation of the isotopic composition of the analysed solutions. The normal sequence of a measurement procedure for one element is therefore:

- blank
- standard (3 injections)
- blank
- unspiked sample (5 injections)
- blank
- standard (2 injections)
- blank
- spiked sample (5 injections)

Due to measuring the standard in two groups (before and after analysing the unspiked sample) it is possible to control the time-stability of the mass discrimination. Significant deviations between the analysed isotopic compositions in the two groups of standard measurements were not observed for all the elements analysed to date, indicating that mass discrimination is nearly stable under constant measurement parameters (gas flow, incident power, lens voltage).

Since the unspiked and the spiked samples are analysed in the same measurement campaign systematic errors of the analytical procedure can be excluded, because both samples are analysed under the same parameters.

For the calculation of the isotopic composition of the different elements the background signal of the eluent has to be subtracted from the signal of each isotope. The resulting net-signal is used for the calculation of the isotopic abundances of each isotope in the unspiked and spiked fuel samples. The mean value of the isotopic composition of each element and the standard deviation are determined from the results of the five individual injections of each sample.

3.3 Quantitative determination of ^{147}Pm by external calibration using HPLC-ICP-MS

As mentioned before ^{147}Pm can not be quantified by isotopic dilution analysis because it is mono-isotopic. Nevertheless, in order to separate the interfering ^{147}Sm from ^{147}Pm a chromatographic separation is necessary. The concentration of ^{147}Pm was determined by external calibration with the ^{147}Pm standard Pm147-ELSB45 (CEA, France) using the on-line coupled HPLC-Q-ICP-MS system. An other possibility for quantification would be the method of standard addition. Unfortunately, the concentration of the ^{147}Pm standard was not high enough for spiking all the fuel samples. The calibration curve for ^{147}Pm was measured in the range of 1 to 4 ng/g solution (see figures 1 and 2). As an internal standard the isotope ^{142}Nd was chosen, because it is not present in high concentrations in fuel samples and it elutes directly in front of ^{147}Pm from the chromatographic column under the conditions used. The added ^{142}Nd concentration was high enough that the error for the internal standard concentration due to the presence of this isotope in the samples can be guaranteed to be < 1 %.
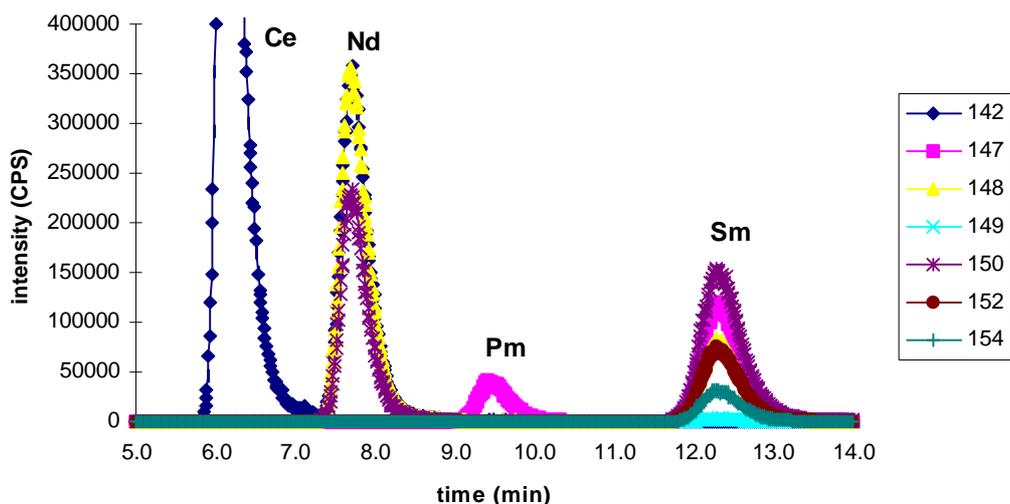
Figure 1: Chromatographic separation of neodymium, samarium, and promethium in an irradiated fuel sample (neodymium was added as internal standard); the ^{147}Pm concentration in this solution is about 4 ng/g

Figure 2 shows the calibration curve for the ^{147}Pm determination in a irradiated nuclear fuel sample gained by the method described above.
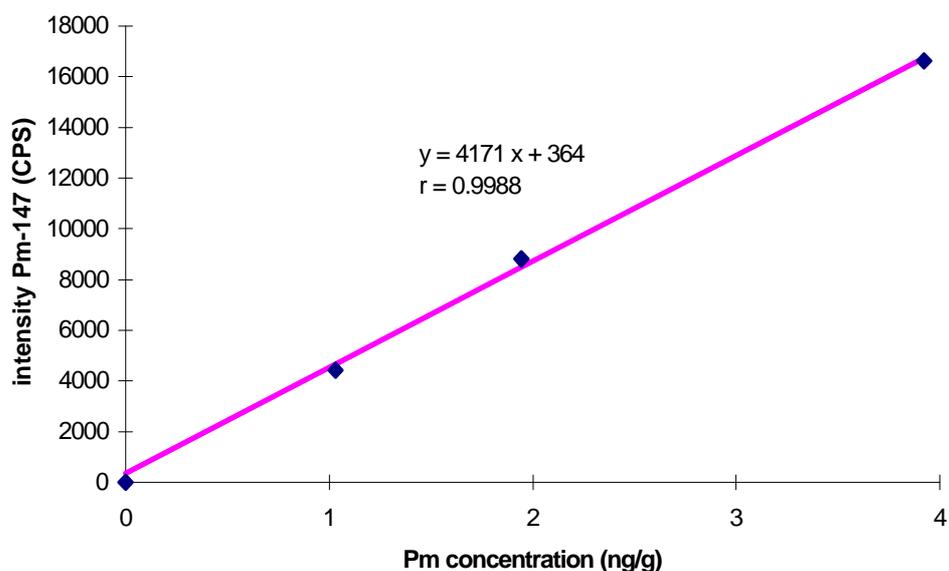

y = 4171 x + 364
r = 0.9988

Figure 2: Calibration curve for ^{147}Pm (external calibration using the HPLC-Q-ICP-MS system)

The determination of a mass discrimination factor is not necessary because ^{147}Pm is mono-isotopic and mass discrimination only influences the measurement of isotopic ratios. The calibration standards and samples were injected three times into the HPLC-ICP-MS system. The ^{147}Pm concentration in the fuel samples was calculated as the mean value of the three injections.

3.4 Precision and Accuracy of the Isotope Ratio Measurements

Typical relative standard deviations (RSD, in %) for the determination of isotopic vectors for the investigated elements are listed in Table 2 for both techniques.

Table 2: External precision of isotope ratio measurements for HPLC-Q-ICP-MS and HPLC-MC-ICP-MS

Isotope abundance (At. %)	HPLC-Q-ICP-MS % RSD	HPLC-MC-ICP-MS % RSD
< 0.1	2 – 10	about 1
0.1 – 1	2 – 5	< 1
1 – 10	1 – 2	< 0.1
> 10	< 1	< 0.05

In order to evaluate the accuracy of an analytical method it is necessary to measure certified reference standards with the same procedure as the samples and to compare the results with the published reference values. The comparison between the reference values for isotope ratios of U and Nd and the measured results for MC-ICP-MS and HPLC-MC-ICP-MS is shown in Table 3.

The data in Table 3 clearly indicate the high accuracy for MC-ICP-MS and even for the online coupled HPLC-MC-ICP-MS where the deviation from the corresponding reference value for U and Nd is only slightly higher.

Table 3: Accuracy of isotope ratio measurements for Nd (LaJolla) and U (NBS-U500) reference materials (the number in brackets corresponds to the absolute standard deviation (1 s); the accuracy is calculated as the deviation from the reference value)

Ratio	Reference value	MC-ICP-MS	HPLC-MC-ICP-MS
$^{143}Nd/^{144}Nd$	0.511858(4)	0.511844(9)	0.511921(38)
accuracy		- 0.003 %	0.012 %
$^{234}U/^{238}U$	0.010422(4)	0.010443(2)	0.010462(66)
accuracy		+ 0.2 %	+ 0.4 %

4   Conclusion

With the online combination of a HPLC and an ICP-MS system it is possible to separate interfering elements and to determine the isotopic composition of these elements in a single analytical procedure. The comparison of the results from Q-ICP-MS and MC-ICP-MS after HPLC separation shows a significant improvement in the analytical precision of the transient data with multicollector detection.

Whereas the analytical performance of a HPLC-Q-ICP-MS system is reduced for isotope ratio measurements because of the sequential detection mode, the HPLC-MC-ICP-MS allows the simultaneous detection of up to nine isotopes and provides therefore highly precise isotope ratio data.

Due to the high diversity of chromatographic resins and eluents of the HPLC (inorganic acids, organic solvents and chelating agents) a separation method for most of the elements of the periodic table can be developed. Online coupled HPLC-ICP-MS systems have a further benefit: the separation of the sample matrix from the analyte elements. Particularly for

the determination of trace elements in a high concentrated matrix, the online separation of matrix elements may lead to significantly lower detection limits, because signal suppression due to high concentrated matrix elements is avoided.

Table 4 summarises the advantages and disadvantages of the mass spectrometric methods used at PSI. ***It is to emphasize that this table is valid specifically for the PSI instrumentation***. Newer quadrupole instruments are much more sensitive, but a quadrupole instrument measures always <u>sequentially</u> whereas a multicollector machine <u>simultaneously</u>.

Table 4: Comparison of the two mass spectrometric methods at PSI

MC-ICP-MS		Q-ICP-MS	
no multielement capability (only one, maximal two elements at the same time detectable)	☹	multi element method (e.g. Li, Zr, …, and internal standard at the same time detectable)	☺
higher response, lower detection limits	☺	lower response, higher detection limits	☹
high precision for isotope ratios	☺	low precision for isotope ratios	☹
high resolution e.g. ^{56}Fe and ^{40}Ar^{16}O distinguishable ($\Delta m = 0.022$ a.m.u.)	☺	low resolution ^{56}Fe and ^{40}Ar^{16}O **<u>not</u>** distinguishable	☹

In figure 3 the precision and the accuracy of different methods are specified. For PSI with a limited manpower it is very important to introduce methods which are time saving and at the same time have a good accuracy and a good precision. Therefore combining an HPLC system with a MC-ICP-MS instrument fits this goal very well.
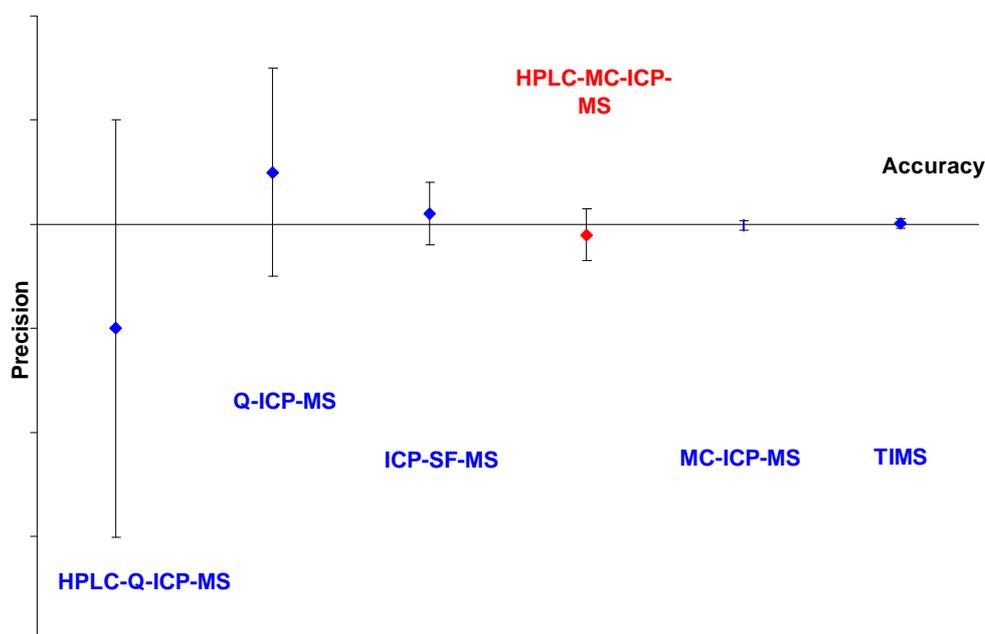

Figure 3: Comparison of the accuracy and the precision of different methods and instrument combinations (SF means sector field)

5   References

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