

# Overcoming present limitations in ICP-MS for iron measurements

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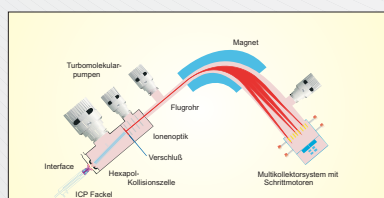
## Intro and Motivation

Iron plays a vital role in human respiration and additionally is a constituent of several enzymes. This makes iron an essential element in human health and thus nutrition. Therefore, iron is subject to various developments and investigations in analytical chemistry.

The early days of inductively coupled plasma mass spectrometry (ICP-MS) lived under the euphoria that nearly all elements can be analyzed easily. However, this optimistic view has changed to a more realistic one and the trouble with several interferences started. Since this time iron stays for elements suffering from molecular interferences.

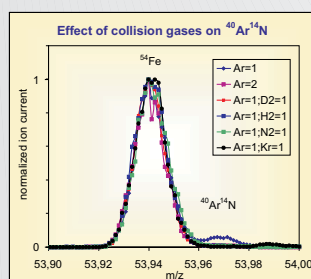
## Applied ICP-MS

In the presented work a multi-collector (MC) ICP-MS equipped with a hexapole collision cell was applied. Figures of merit will be compared to those of other ICP-MS instruments, results will be compared to TIMS.



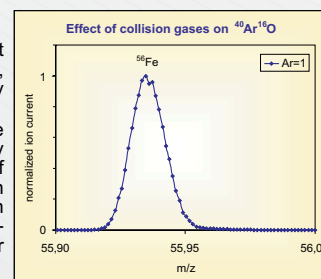
## Fe-interfering species in ICP-MS

The biggest problem in iron measurements using ICP-MS is the variety of interferences. Isobaric interferences such as Cr can be corrected mathematically by measuring another undisturbed isotope of the interfering element. This can be applied best by using a multi-collector ICP-MS allowing simultaneous measurements. Contrary the more frequent interfering molecular ions like ArN, ArO, ArOH and CaO are more difficult to correct for, as their formation strongly depends on the sample matrix. Moreover in most cases a suitable isotope for corrections is missing. The main strategies to overcome these interferences are high resolution, collision cells and cool plasma.



## <sup>54</sup>Fe and <sup>40</sup>Ar<sup>14</sup>N

Already the use of Ar or mixtures like Ar/H<sub>2</sub> as collision gases completely remove the <sup>40</sup>Ar<sup>14</sup>N interference, as displayed on the left (resolution ~3000, 10 ng·g<sup>-1</sup> Fe). The isobaric interference <sup>54</sup>Cr can be corrected mathematically by measuring <sup>52</sup>Cr. Further investigations proved the combination of Ar/H<sub>2</sub> sufficient to completely remove the <sup>40</sup>Ar<sup>14</sup>N interference even at levels of 1% Methanol.



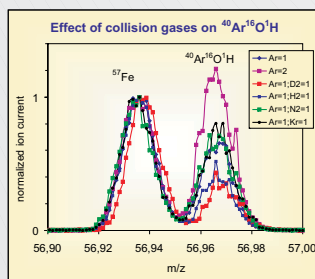
## <sup>56</sup>Fe and <sup>40</sup>Ar<sup>16</sup>O

Unfortunately the main abundant isotope of Fe, <sup>56</sup>Fe, simultaneously is the most heavily interfered Fe-isotope. This most disturbing interference of <sup>40</sup>Ar<sup>16</sup>O however is completely removed by nearly any setting of the collision cell. The picture on the right shows a high resolution (~3000) mass scan of a Fe-solution containing 10 ng·g<sup>-1</sup>. Ar was applied as collision gas.

## <sup>57</sup>Fe and <sup>40</sup>Ar<sup>16</sup>O<sup>1</sup>H

The <sup>40</sup>Ar<sup>16</sup>O<sup>1</sup>H-interference turned out to be much more stable and resistant than the <sup>40</sup>Ar<sup>14</sup>N- and the <sup>40</sup>Ar<sup>16</sup>O-interference.

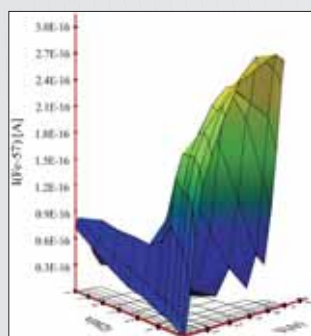
The picture on the right displays a selection of high resolution (~3000) mass scans for different collision gas settings. The sample contained 10 ng·g<sup>-1</sup> Fe as before. The ratio of the <sup>57</sup>Fe and the <sup>40</sup>Ar<sup>16</sup>O<sup>1</sup>H peak area is ~2 when applying 1 mL·min<sup>-1</sup> Ar as collision gas. Increasing the Ar flow rate or adding Kr or N<sub>2</sub> will decrease or downgrade this ratio to values <1. Best results (ratios ~3) were gained by adding 1 mL·min<sup>-1</sup> H<sub>2</sub> or D<sub>2</sub>, whereas D<sub>2</sub> gives always higher ratios than H<sub>2</sub>.



## <sup>57</sup>Fe and <sup>40</sup>Ar<sup>16</sup>O<sup>1</sup>H

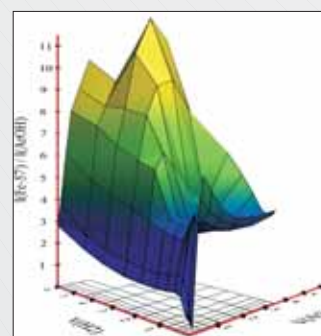
The increase of the Ar flow rate leads to an increase of the <sup>40</sup>Ar<sup>16</sup>O<sup>1</sup>H signal. In addition the use of D<sub>2</sub> as collision gas provides the best results, lowest <sup>40</sup>Ar<sup>16</sup>O<sup>1</sup>H-signal. These facts could possibly be explained by an at least partial formation of the <sup>40</sup>Ar<sup>16</sup>O<sup>1</sup>H-interference within the collision cell. This also could explain, why D<sub>2</sub> provides better results than H<sub>2</sub>.

A reduction of oxygen and hydrogen could lead to further improvements. The application of an MCN with desolvation unit however could not reduce the interference further but lead to drastic cross-contamination effects.



## Signal-to-interference-ratio for <sup>57</sup>Fe

The favourable combination of Ar/H<sub>2</sub> could be improved by optimizing not for maximum signal intensity but for maximum signal-to-interference-ratio. For this purpose more than 100 high resolved mass spectra were measured for different Ar/H<sub>2</sub> flow rates (Fe 10 ng·g<sup>-1</sup>). The picture on the left displays the results for the signal intensity on mass 57 in form of a 3D graph, the picture on the right displays the results for the signal-to-interference-ratio <sup>57</sup>Fe/<sup>40</sup>Ar<sup>16</sup>O<sup>1</sup>H. The optimum signal-to-interference-ratio gives only 4% of the maximum possible signal on 57. Therefore in most cases a compromise between highest signal intensity and optimum signal-to-interference-ratio has to be found. In this work an Ar flow of 1.8 and a H<sub>2</sub> flow of 0.8 mL·min<sup>-1</sup> was found the best compromise, resulting in ~71% of the maximum signal and still 30% of the optimum signal-to-interference-ratio.



## Figures of Merit

Fe measurements	Instrument		
	MC-ICP-MS	DRC-ICP-MS	HR-ICP-MS
Isotope ratio <sup>54</sup> Fe/ <sup>56</sup> Fe	0.05805		
u (n=1, 5 min)	0.01	0.16 [1]	< 0.1 [1]
u (n=24, 10h)	0.01	0.20 [1]	< 0.1 [1]
Isotope ratio <sup>57</sup> Fe/ <sup>56</sup> Fe	0.02414		
u (n=1, 5 min)	0.02	0.14 [1]	< 0.1 [1]
u (n=24, 10h)	0.02	0.08 [1]	< 0.1 [1]
Intensity <sup>56</sup> Fe in Mcps per μg·g <sup>-1</sup> Fe	1500 (1.2 V at 50 ng·g <sup>-1</sup> Fe)	40 [2]	200 (LR) [3] 5 (MR)

## Applying IDMS for Fe certification measurements

The development of highly accurate and precise procedures for Fe isotope ratio determinations reached a performance level, which is far beyond that of other instruments. Applying the developed measurement procedures on certification measurements by using IDMS results for water, tea leaves and polish herbs samples were achieved which agree very well with the reference values within their uncertainties.

Certification	Unit	Fe content		Reference type
		MC-ICP-MS	Reference	
IMEP-12	nmol·g <sup>-1</sup>	3.850 ± 0.022	3.805 ± 0.091	Certified Value
Tea Leaves INCT-TL1	mg·kg <sup>-1</sup>	542 ± 11	541 ± 12	TIMS (this work)
Mixed Polish Herbs INCT-MPH2	mg·kg <sup>-1</sup>	543 ± 12	541 ± 13	TIMS (this work)

[1] JAAS, 2002, 17, 933-943; [2] JAAS, 2000, 15, 1261-1269; [3] Anal Chim Acta, 1998, 367, 183-191

Due to analyte/matrix separation and collision cell technology CaO-interferences could not be observed.