

focus on Mass Spectrometry & Spectroscopy

New Fields of Application Thanks to Innovative HR-CS Spectrometers

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Development of high resolving HR-CS spectrometers

Atomic absorption spectrometers (AA spectrometers) are used in a variety of analytical laboratories. The main advantages of AA spectrometers are their high selectivity and specificity combined with their ease of use. Conventional AA spectrometers are limited by the following restrictions:

- simultaneous determination of several elements is not possible.
- changing the hollow cathode lamps when analysing different elements is time consuming.
- determination of non-metals is not possible.
- the analysis of elements in matrix samples causing spectral band overlap requires additional effort.

New high-resolution continuum source absorption spectrometers (HR-CS spectrometers) are based on the results of fundamental research by Becker-Ross and co-workers at ISAS Berlin and developed by Analytik Jena AG in cooperation with this research group. They are currently only manufactured and sold by Analytik Jena AG and represent a further development of AA spectrometers, eliminating the disadvantages of traditional instruments while retaining their benefits mentioned above. The radiation source of an HR-CS spectrometer is a xenon short-arc lamp that emits a continuum in the wavelength range of 185 to 900 nm. The radiation is transmitted in high resolution in a double monochromator, consisting of a prism and an Echelle grating, and then registered by means of a CCD array. The result is time-resolved and wavelength-resolved spectra, which can be used to gain significant data with respect to the composition of the sample and possible interference caused by matrix components.

Simultaneous Determination of Several Elements

The wavelength-dependent resolution of the HR-CS spectrometer means it is possible to register a range of 0.2 nm (at $\lambda = 190$ nm) to 0.6 nm (at $\lambda = 700$ nm). If the analysis wavelengths of two or more elements fall within this spectral window and if the atomising temperatures of the elements being examined are not too different, they can be determined simultaneously. An example of the simultaneous analysis of two elements is the determination of iron and chromium in aqueous solution, since one of the many iron absorption lines is located near the chromium resonance line (see Figure 1).

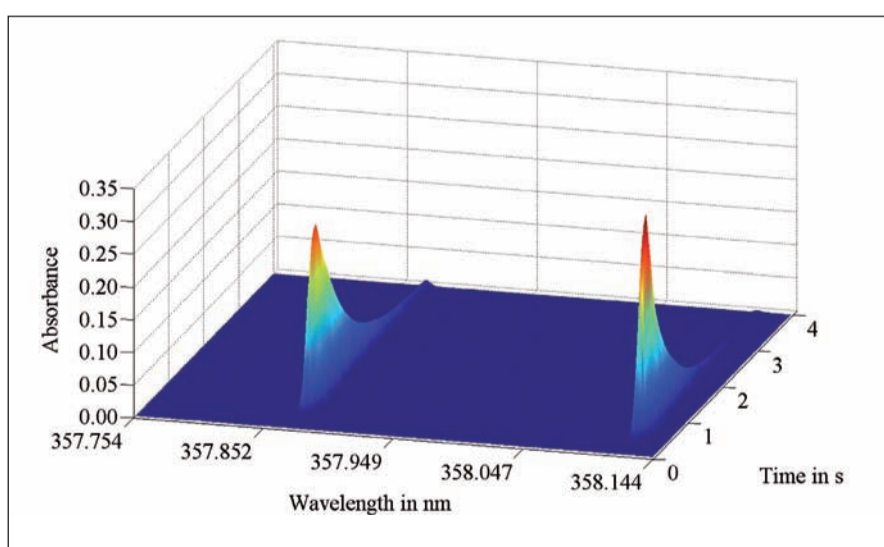


Figure 1: Simultaneous determination of chromium and iron

Other examples for the simultaneous and sequential analysis of elements are described in the literature, applying both flame as well as graphite furnace techniques as atomising method [1, 2].

Determination of Non-Metals

Direct determination of non-metals was – and still is – only possible to a limited extent with conventional AA spectrometers and with HR-CS spectrometers, because the resonance wavelengths of non-metals are below 190 nm. Firstly, there is a lack of suitable radiation sources and secondly oxygen absorbs in this spectral range, so that a vacuum monochromator is required. As a result the determinations in routine use are unprofitable.

One alternative is molecular absorption spectroscopy (MAS), since diatomic molecules also absorb in the wavelength range of 185 to 900 nm. The molecule, consisting of the non-metal being examined and a binding partner (metal or other non-metal), is formed either in the flame or in the graphite tube. Molecular absorption measurements for the analysis of non-metals have already been carried out with conventional AA spectrometers [3]. The performance of these determinations, however, was limited by the use of lower intensity deuterium lamps. Hollow cathode lamps of various elements have also been used as a radiation source, where the maximum molecule absorption peak rarely coincided with the maximum of the emission peak of the hollow cathode lamp, which results in a lower sensitivity and a poorer detection limit.

In the case of HR-CS spectrometers the xenon short-arc lamp emits radiation in the range of 185 to 900 nm with high radiation intensity, so that each wavelength in this range can be used to analyse the rotational bands of the molecules. Furthermore, the double monochromator and the CCD array mean it is possible to detect the fine rotational structure of the molecular bands to a high resolution.

The procedure of analysing non-metals via molecular bands, as shown in the following examples, is transferable to further determinations of other non-metals or molecules.

Fluorine

The stable binding of fluorine to most elements means a variety of molecules are possible, provided these absorb in the emission profile of the xenon short-arc lamp. Diatomic molecular compounds with elements of the third main group of the periodic system, such as aluminum and gallium, are ideally suited to the quantitative analysis of fluorine since these molecules are stable at temperatures of about 2000°C.

Gallium fluoride is formed in the graphite tube after injection of 500 µg of gallium and the fluoride-containing solution. The absorption maximum of GaF is at 211.248 nm. The graphite tube is coated with zirconium, pre-treated with the Pd/Mg modifier and sodium acetate is added to stabilise the elements used and to suppress interaction effects with the graphite. After these optimisation steps, a detection limit for fluorine of 5.2 pg (corresponding to 0.52 µg/L at 10 µL injection volume) was achieved [4]. The developed method is used inter alia in the quantitative analysis of total fluorine content and the soluble F content in toothpaste. The advantages of HR-CS spectrometers include the ease of use and time savings compared to other methods [5].

Bromine

Bromine can also be determined via different molecules, where potential binding partners are elements of the second and third main group in particular. In this way, bromine was quantitatively determined via calcium bromide bands at 625.315 nm (see Figure 2).

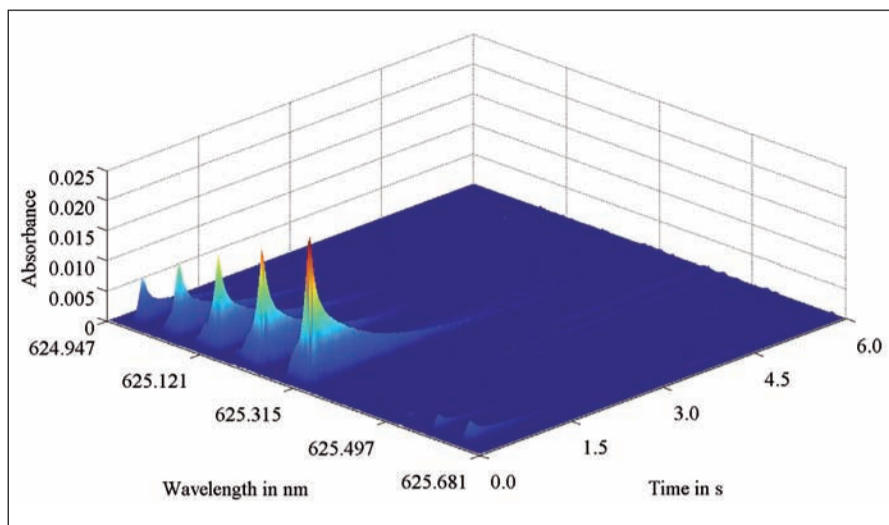


Figure 2: CaBr rotational spectrum

Similar to the determination of fluorine, the molecular formation reagent is injected into the graphite tube in excess (2% m/v calcium) together with the bromide-containing solution. The coating of the graphite tube and the additional use of the Pd/Mg modifier are also advantageous because then reproducible and intensive CaBr absorption signals are obtained. In addition, the use of graphite tubes without integrated PIN platform has proven effective with respect to lower detection limits, since the evaporation of the substances is not delayed, but rather happens very quickly from the tube wall outwards and thus the formation of molecules occurs rapidly.

The linear working range of the method extends over six orders of magnitude, because, as can be seen in Figure 2, less intense peaks can be used for the analysis. The detection limit of the method is 78 pg Br (corresponding to 7.8 µg/L Br at 10 µL injection volume). However, the determination of bromine is limited by competing reactions in the graphite tube, caused by chloride, fluoride, aluminium or iron, which can also form stable compounds with calcium and bromine. For this reason, the quantitative analysis of bromine is limited to small matrix samples or time-consuming methods have to be applied, such as the standard addition [6].

Sulphur

Sulphur forms stable molecules that are particularly well suited to its quantitative analysis with elements of the fourth main group of the periodic system. Other diatomic molecular compounds are also possible.

In the case of the determination of sulphur, tin solution (10 g/L Sn in 6% HCl) injected in excess into the graphite tube is required to form the molecule. A sodium sulphate solution is used as a sulphur standard for calibration. The reducing conditions in the graphite tube mean the corresponding sulphide is always formed.

The determination of sulphur via tin sulphide bands is a sensitive and robust method [7]. The pronounced rotational fine structure of the SnS bands is particularly noticeable in this context (see Figure 3).

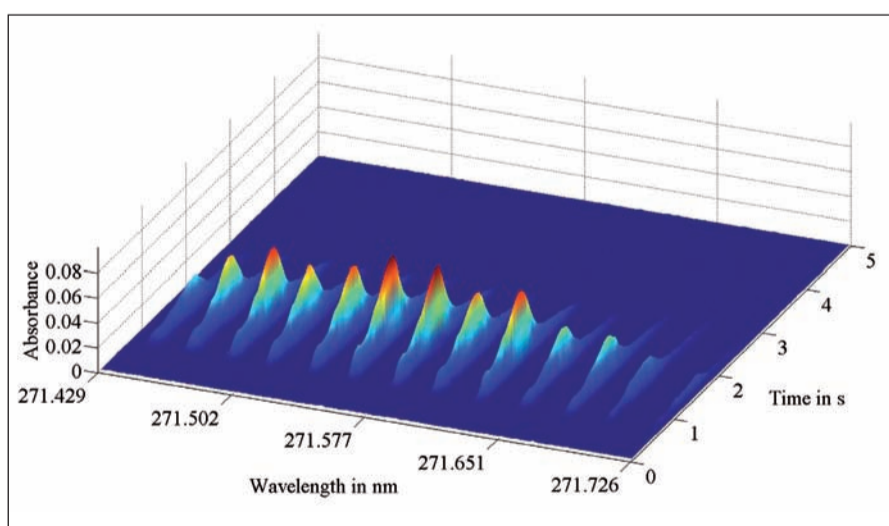


Figure 3: SnS absorption spectrum

Similar to the analysis of bromine, the best results in graphite tubes are obtained without integrated PIN platform. The detection limit of the method is 0.16 ng sulphur (corresponding to 16 µg/L sulphur at 10 µL injection volume). The performance and robustness of the method is mainly reflected in the fact that no other elements except nickel cause interference in the determination of sulphur via SnS bands. In contrast to the analysis of bromine, sulphur can be determined in various matrices, such as river, pond and mineral water samples. The accuracy of the results in the determination of sulphur via SnS bands using an HR-CS spectrometer was additionally confirmed by ion chromatography and gravimetry [7].

Using HR-CS spectrometers it is also possible to quantitatively determine non-metals in addition to metals and semi-metals. This represents a further advantage of HR-CS spectrometers in addition to the simultaneous determination of several elements.

Application in Species Analysis

In modern analytics, the quantitative determination of the total concentration and the total content respectively of metals is still important, although the analysis of individual element species is increasingly relevant. The occurrence, the binding form, the oxidation state and stability of the corresponding compound are of particular interest in this type of analysis. One recent example is the analysis of arsenic species (see Figure 4) in human matrices. The inorganic arsenic compounds arsenite [As(III)] and arsenate [As(V)] are classified as carcinogenic, the organic species monomethylarsonic acid [MMA(V)] and dimethylarsonic acid [DMA(V)] are debated as cancer promoters, whereas arsenobetaine [AsB] is considered non-toxic, but quantitatively the most abundant for example in marine organisms. An indication of the As total content cannot be used to draw any conclusions on the toxicity, since in general the proportion of each toxic As species does not correspond to the As total content.

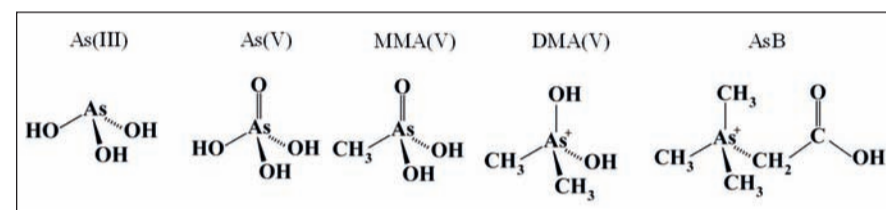


Figure 4: Important arsenic species

The analysis of As species is generally accomplished by coupling a separation technique with a sensitive detector. Coupling liquid chromatography with a HR-CS spectrometer is a new, innovative method. Using a highly efficient hydrophobic anion exchange column, the As species As(III), As(V), MMA(V), DMA(V) and AsB can be separated within 7 minutes under the conditions indicated in Table 1 [8].

Table 1: Conditions of anion exchange chromatography

Precolumn	IonPac AG7 (4 mm x 50 mm, 10 µm) by Dionex
Separation column	IonPac AS7 (4 mm x 250 mm, 10 µm) by Dionex
Flow rate	1.3 mL · min ⁻¹
Mobile Phase A	0.4 mM HNO ₃ ; 0.25 mM MeOOH
Mobile Phase B	50 mM HNO ₃ ; 0.25 mM MeOOH
Gradient program	0.00 – 1.85 100% A v/v 1.86 – 2.75 90% A; 10% B (linear) v/v 2.76 – 3.50 50% A; 50% B (linear) v/v 3.51 – 7.00 50% A; 50% B v/v 7.01 – 12.00 100% A v/v
Temperature	30°C

An offline coupling is used to collect the individual fractions of the anion-exchange chromatography in the autosampler of the HR-CS spectrometer every 6 seconds. These are then analysed in the graphite tube. Plotting the absorbance of each fraction over time results are shown in the chart in Figure 5.

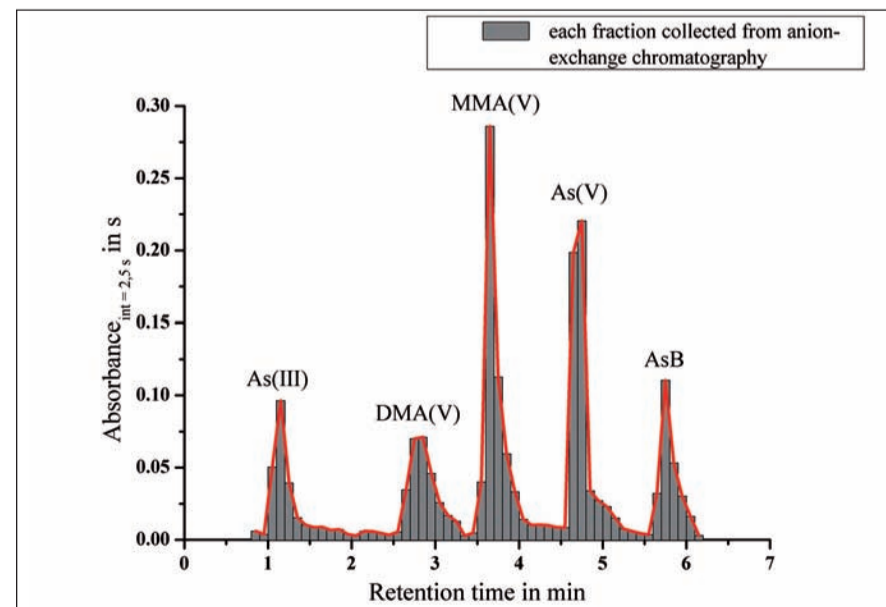


Figure 5: Chart obtained by plotting the absorbance of each fraction for the separation of five arsenic species using anion exchange chromatography and an HR-CS spectrometer as detector

As can be seen from Figure 5, ten fractions of anion exchange chromatography are obtained per minute, corresponding to a volume of 120 μL per fraction at a flow rate of 1.2 mL/min.

Due to the different binding forms, calibration series were recorded for both the inorganic and organic arsenic species. The method is more sensitive to the organic species than the inorganic. Furthermore, lower detection limits (see Table 2) were achieved for the organic compounds MMA(V), DMA(V) and AsB.

Table 2: Analytical parameters for the analysis of arsenic using HR-CS AAS

Parameters	Inorganic Arsenic	Organic Arsenic
Analysis via	Height (5 pixels)	Height (5 pixels)
Detection limit* in $\mu\text{g}\cdot\text{L}^{-1}$	0.45	0.31
Determination limit* ($k = 3$) in $\mu\text{g}\cdot\text{L}^{-1}$	1.40	0.94
Relative method standard deviation in %	5	6

* Determination according to DIN 32645 (significance level for type 1 error = 0.05)

It was also possible to increase the sensitivity by using several pixels for the analysis of the absorption signal.

Interference Correction for Complex Matrices

HR-CS spectrometers are particularly suited for the determination of arsenic in human matrices, such as urine or blood. Phosphates and chlorides in particular, which are found primarily in these matrices, also form stable molecules in the graphite tube. The molecular bands extend over a wavelength range in which, among other things, the arsenic resonance line is at 193.695 nm. The wavelength-resolved and time-resolved detection means these molecular bands are identified and can then be corrected, as is demonstrated below for the determination of arsenic in the presence of phosphate (Figure 6 – Figure 7).

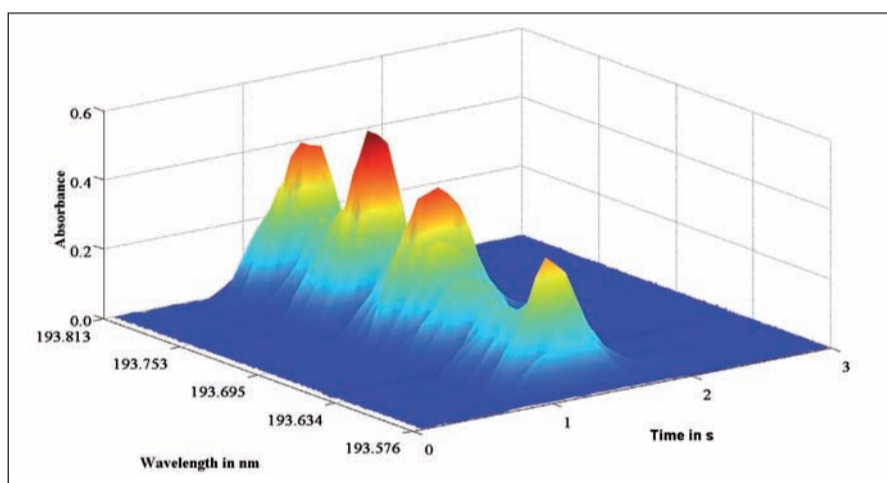


Figure 6: PO rotational band in the presence of the As resonance line at 193.695 nm

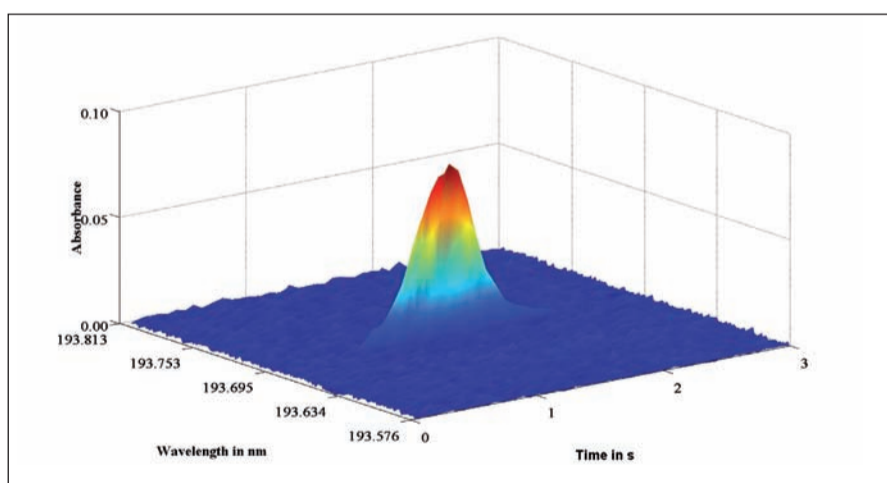


Figure 7: As absorption spectrum after spectra correction

With phosphate contents in the mmol/L range, such as in urine, there is a signal superposition of the As resonance line caused by PO molecular bands (Figure 6), whereby a higher absorbance signal is obtained at this wavelength. With precise knowledge of the composition of the matrix or the interfering substance, this can be used as a reference substance or correction substance. In the example cited, the PO correction spectrum is then subtracted from the original spectrum (Figure 6), so a corrected arsenic absorption peak (Figure 7) is obtained as a result.

Coupling anion exchange chromatography with an HR-CS spectrometer is a fast and easy way to quantitatively determine arsenic species in matrix samples. Compared to ICP-MS

instruments, some advantages of HR-CS spectrometers that can be cited are primarily the lower cost in terms of purchase and maintenance, and the correction of spectral interferences.

Summary and Outlook

The new innovative HR-CS-spectrometers open up new areas of application for the user, in addition to traditional metal/semi-metal analysis. These areas include the simultaneous determination of two or three elements or the determination of non-metals via high-resolution molecular rotation bands.

One new practical application is to couple the HR-CS spectrometer with anion exchange chromatography, whereby the five arsenic species of arsenite, arsenate, monomethylarsonic acid, dimethylarsinic acid and arsenobetaine can be separated and quantified. The effective spectra correction in particular permits analysis of the individual species in the presence of interfering substances such as phosphate that cause spectral interference. After successful optimisation of both the chromatographic separation and the HR-CS AAS method, the five arsenic species can be separated and detected within 7 minutes, where detection limits in the lower $\mu\text{g/L}$ range can be achieved.

High-resolution continuum source spectrometers are much more versatile than traditional atomic absorption spectrometers and especially inexpensive and simple to use compared to other analytical techniques.



Figure 8: HR-CS AAS contrAA®

Acknowledgments

The authors thank the Analytik Jena AG for providing the high-resolution atomic absorption spectrometer contrAA® 700 and the company Recipe® for providing the HPLC system.

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