Review

Continuum Source Atomic Absorption Spectrometry: Past, Present and Future Aspects – A Critical Review

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Este artigo de revisão aborda 1½ séculos de história da espectrometria de absorção atômica com fonte contínua (CS AAS), partindo dos primeiros experimentos de Kirchhoff e Bunsen nos anos 1860. Ele também tenta explicar porque a técnica foi abandonada na primeira metade do século XX, porque ela foi redescoberta nos anos 60 nos EUA, onde vários grupos de pesquisa trabalharam intensamente no desenvolvimento da CS AAS por cerca de quatro décadas e, finalmente, não obtiveram sucesso. Esta revisão também discute as principais vantagens da moderna técnica de CS AAS de alta resolução (HR-CS AAS), que usa um monocromador duplo de alta resolução e um detector com arranjo de dispositivos de carga acoplada, o qual adiciona o comprimento de onda como terceira dimensão. A literatura sobre as aplicações de HR-CS AAS foi cuidadosamente revisada. Finalmente, será feita uma tentativa de prever os avanços futuros desta técnica nova e antiga.

This review article covers 1½ centuries of history of continuum source atomic absorption spectrometry (CS AAS), starting with the early experiments of Kirchhoff and Bunsen in the 1860s. It also tries to explain why the technique was abandoned in the first half of the 20th century, why it was "re-discovered" in the 1960s in the USA, where several research groups worked intensively on the development of CS AAS for about four decades, and why they finally failed. This review also discusses the major advantages of modern high-resolution CS AAS (HR-CS AAS), which uses a high-resolution double monochromator and a charge coupled device array detector, which adds the wavelength as third dimension to the usual display of absorbance over time. The literature about applications of this technique has been carefully revised. Finally an attempt will be made to foresee future developments of this technique, which is obviously not an easy task.

Keywords: history of continuum source AAS, background correction, non-metals determination, multi-element determination, direct solid sample analysis

1. The Early History

In the 1850s coal gas was introduced in the city of Heidelberg, Germany, for illumination of the streets, and Robert W. Bunsen (1811-1899), professor of Chemistry at the University of Heidelberg, succeeded to connect his laboratory to this gas supply. Soon after he invented the well-known Bunsen burner, the first burner in which the fuel was pre-mixed with air before it was ignited, producing a hot and non-luminous flame, which facilitated significantly the observation of atomic spectral lines. Soon after, as kind of a confirmation of the usefulness of his burner, Bunsen discovered the elements rubidium and cesium in mineral water and also succeeded to isolate them. Towards the end of the 1850s, Gustav R. Kirchhoff (1824-1887), professor of Physics at the same university, became interested in the experiments of Bunsen, which should be the beginning of a life-long cooperation between

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the two scientists. Their joint research included a detailed comparison of the emission spectra obtained with pure salts with the black lines observed in the sun's spectrum and with absorption spectra produced in their lab. As a result of this research, Kirchhoff[1] published his basic manuscript about the connection between absorption and emission of radiation, postulating that "any material that can emit radiation at a given wavelength can also absorb radiation of that wavelength".

Obviously, all the spectroscopic experiments that were carried out in the 19th century were in the visible range using spectroscopes and observation with the naked eye; continuum radiation sources, such as electric arcs, were used for absorption measurements, as these were the only reliable emission sources at that time.[2] Towards the end of the 19th century and at the beginning of the 20th century the ultraviolet (UV) range of the spectrum was discovered, and an intense research and development of monochromators and polychromators for atomic spectroscopy started in order to explore this spectral range. Around 1925 the first commercial atomic spectrometers became available using arcs and sparks as the emission sources and photographic plates for the detection and quantitative determination of metallic elements in the visible and UV range. Emission spectroscopy was obviously the preferred technique as it was easier to detect a small emission signal in an otherwise dark and non-luminous environment than a small reduction of the radiation over a narrow spectral range within a bright, luminous environment, as it would be for absorption measurements. Hence, atomic absorption was practically abandoned during the first half of the 20th century.

2. Introduction of Line Source AAS

This situation only started to change in the second half of the 20th century when Alan Walsh, who had worked at the Commonwealth Scientific and Industrial Research Organization (CSIRO) in Australia for several years, first with molecular spectroscopy and then with atomic spectroscopy, started to wonder why absorption is generally used in molecular spectroscopy and emission in atomic spectroscopy. The result of his musing was that "there appeared to be no good reasons for neglecting atomic absorption spectra; on the contrary, they appeared to offer many vital advantages over atomic emission spectra as far as spectrochemical analysis was concerned".[3] At the same time, however, Walsh also realized one of the main difficulties of atomic absorption "that the relations between absorption and concentration depend on the resolution of the spectrograph, and on whether one measures peak absorption or total absorption as given by the area under the

absorption/wavelength curve".[3] He therefore precluded the use of continuum sources for the measurement of atomic absorption spectra, as in this case a resolution of about 2 pm would be required, which was far beyond the capabilities of the best spectrometers available at that time.

This realization led Walsh to conclude that the measurement of atomic absorption requires line radiation sources with the sharpest possible emission lines, i.e., hollow cathode lamps (HCL). The task of the monochromator is then merely to separate the line used for the measurement from all the other lines emitted by the source. The high resolution demand for atomic absorption measurements is in this case provided by the line source. Walsh also postulated that the radiation source should be modulated and a synchronously tuned detection system be used. This way any radiation emitted by the sample in the atomizer produces no signal at the output of the detection system. The first publication of Alan Walsh, where he proposed the application of atomic absorption spectra to chemical analysis, appeared at the beginning of 1955;[4] however, the success was not spontaneous. In spite of the tremendous effort that Walsh and his colleagues made to "sell" atomic absorption, there was only a very small group of scientists that was using the new technique. Part of the problem was for sure that the first commercially available instruments did not include the modulation principle, one of the key features postulated by Walsh for proper performance of the technique.

The break-through finally came in 1962, when Walsh presented the technique and the results obtained by a few laboratories in Australia to various members of the staff of the Perkin-Elmer Corporation in Norwalk, CT, USA. It was during these discussions that Chester Nimitz, the then-General Manager of the Instrument Division, asked rather tersely: "If this goddam technique is as useful as you say it is, why isn't it being used right here in the USA?" The response of Alan Walsh: "This is due to the effect that the USA, to a certain extent, is an underdeveloped country" must have had a significant impact, as the decision of Perkin-Elmer to embark on a large-scale project related to the production of atomic absorption equipment was made shortly afterwards – the beginning of about half a century of success of line-source AAS (LS AAS).

3. Research on Continuum Source AAS in the USA

However, in spite of the commercial success of LS AAS, there appeared another trend at the same time in the USA, i.e., an intensive research about continuum source AAS (CS AAS). American friends told me that there is a

significant number of their compatriots who are convinced that all important inventions are made in the USA, and anything that comes from outside is considered as "not invented here" (NIH). Maybe this attitude also had some contribution to the search for alternatives to LS AAS in the USA. In the same year, when Walsh presented AAS to Perkin-Elmer, he also had an invited lecture at the Xth Colloquium Spectroscopicum Internationale, organized in Baltimore, MD, USA; it is of importance to note that the chairman of this session was Velmer A. Fassel from the Iowa State University, Ames, IA, who introduced later the inductively coupled argon plasma (ICP) for optical emission spectrometry (OES).[5] In the same session, a William E. Grossman from the Cornell University, Ithaca, NY, gave an oral presentation with the title: "The use of continuous sources instead of hollow cathode tubes in atomic absorption spectroscopy".[6] In their abstract the authors wrote: "The absorbancy of a metal vapor in a flame is higher with a hollow-cathode tube than a continuous source using a conventional monochromator. However, there are many other factors that contribute to sensitivity besides the absorbancy. The stability of the source, for example, determines the level of absorption that can be detected and is an important parameter. Since tungsten sources can be better stabilized than hollow-cathode tubes, some of the loss in sensitivity, caused by the lower absorption, is recovered by the ability to observe smaller changes".[6] Independent on the fact that the authors confused sensitivity with signal-to-noise ratio (SNR), they used the at that time still very poor quality of HCL to demonstrate that Walsh had not considered all aspects, and the use of continuum radiation sources might be the best approach for measuring AAS.

Fassel and Mossotti published their first manuscript on CS AAS soon after,[7] and a few years later a paper, entitled "Evaluation of spectral continua as primary sources in atomic absorption spectroscopy" was published, co-authored by Fassel and Grossman and a few others from the Iowa State University;[8] apparently, Fassel had invited Grossman to continue his research about CS AAS at his university. In the abstract the authors claimed that "for 32 elements, the sensitivities observed for a spectral continuum primary source were either comparable to, or exceeded those presently obtained with sharp-line primary sources". Going through the manuscript it becomes obvious that the authors one more time confused sensitivity with SNR, as they were actually comparing limits of detection (LODs). The table, in which they compare the LOD for 43 elements, is divided in three parts; part A shows 11 elements, for which the LOD using HCL is more than an order of magnitude better. A closer look at this part of the table shows that for five of the elements (Bi, Co, Fe, Ni and Pb) less sensitive lines above 280 nm had to be used for the continuum source, which had little intensity in the spectral range below 300 nm. In addition, a number of important elements, such as As, Be, Cd, Sb, Se and Zn, are not in the list at all, as these elements have no sensitive lines at all above 280 nm. Part B of the table shows 16 elements with comparable LOD, where 'comparable' was defined by the authors as being within the same order of magnitude, and no comment was given on this part. Part C, finally, lists other 16 elements, for which the LOD obtained with a continuum source was more than an order of magnitude better than with a line source. However, most of the elements listed here were rare-earth elements for which no HCL, and hence no data, were available at that time – and a comparison with non-existing data is not possible. In addition, three LOD for HCL were taken from a thesis, where the LOD was defined as the analyte concentration that absorbs 5% of the incident light, which corresponds to five times the characteristic concentration, and has nothing to do with a LOD. In essence, this publication is highly biased towards the use of continuum sources; a realistic comparison should show at least 17 elements with better LOD for HCL and only three elements with better LOD using the continuum source.

This initial research created significant interest in the subject in the USA, resulting in several publications about CS AAS,[9-14] the majority of which came from the group of Winefordner. However, around the mid 1970s a movement started, which was pioneered by Keliher at the Villanova University, PA,[15] and soon after picked up by O'Haver at the University of Maryland,[16] considering in more detail the instrumental requirements for CS AAS. It was finally James M. Harnly who conducted all the research for the next 20 years, investigating all kinds of radiation sources, mono- and polychromators, detectors and evaluation principles for CS AAS.[17-34] Harnly and colleagues also described the first, and up to now only, truly simultaneous multi-element atomic absorption spectrometer with a continuum source.[17,19,22,23] The only other 'simultaneous' CS AAS instruments described in the literature used photodiode array detectors that covered a range of only a few nanometers, and only elements that had absorption lines falling within this narrow spectral window could be detected simultaneously.[35,36]

In 1989 Gary M. Hieftje[37] wrote in a kind of a provocative article that "clearly, for AAS to remain viable in the face of strong competition from alternate techniques will require novel instrumentation or approaches. Among the novel concepts that have been introduced are those involving continuum sources and high-resolution spectral

sorting devices, … and entirely new detection approaches". Hieftje was probably thinking about the work of Harnly when he wrote these sentences, as the various instruments assembled by his group seemed to have all the elements to meet the requirements put out by Hieftje. Nevertheless, the research of Harnly did not call the attention of any instrument manufacturer, maybe in part because he used exclusively components that were commercially available and obviously not optimized for the purpose.

4. Research on CS AAS in Germany

In the meantime, however, a research group at the Institute for Spectrochemistry and Applied Spectroscopy (ISAS) in Berlin, Germany, under the leadership of Helmut Becker-Ross became interested in the research of Harnly. In contrast to Harnly, however, the group at ISAS, Berlin, was all physicists with considerable experience in the design of spectrometers for various purposes. They therefore started to think about the special requirements of CS AAS, investigating different types of radiation sources[38,39] and spectrometer designs,[40] and finally, in 1996, they proposed a completely new spectrometer concept,[41,42] consisting of a Xenon short-arc lamp operating in a hot-spot mode, a compact high-resolution double monochromator with a prism pre-monochromator and an echelle grating monochromator for high resolution, and a linear charge-coupled device (CCD) array detector, as shown schematically in Figure 1. The same group also developed an echelle spectrograph for the simultaneous determination of an unlimited number of elements in the range between 200 and 450 nm, using a flame atomizer,[43] and published several papers about fundamental aspects of instrumentation for continuum source AAS.[44-46]

In a review article, published in 1999, with the title "The future of atomic absorption spectrometry: a continuum source with a charge coupled array detector" Harnly wrote that "the future appears bright for CS AAS. Whereas previously, CS AAS was striving for parity with LS AAS, it is now reasonable to state that it is CS AAS which is setting the standard".[47] However, neither in this publication nor in any of the future manuscripts,[48,49] Harnly cited any of the publications of Becker-Ross and colleagues.

5. Commercial Instrumentation

Finally, at the end of the 20th century, instrument manufacturers got interested in the design of the group of Becker-Ross; the first commercial instrument, the contrAA 300, was introduced by Analytik Jena (Jena, Germany) in 2004, and nowadays we already have a
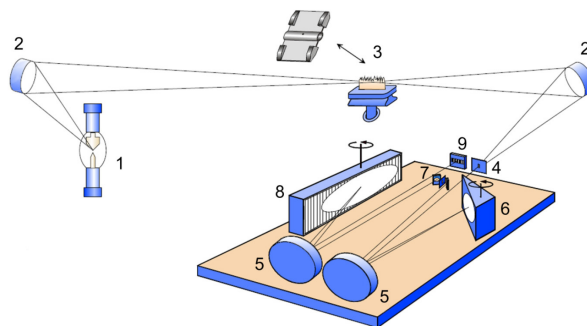

Figure 1. HR-CS AAS setup with high-resolution double monochromator spectrometer; 1: xenon short-arc lamp, 2: elliptical mirrors, 3: atomizer, 4: entrance slit, 5: parabolic mirrors, 6: prism, 7: folding mirrors and intermediate slit, 8: echelle grating, 9: CCD detector; (from reference 50; copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission).

whole family of high-resolution continuum source atomic absorption spectrometers (HR-CS AAS). No details of these instruments will be given here, as they were published in a monograph and several articles and book chapters.[50-54] It should only be mentioned that the resolution *per* pixel is about 1.5 pm at 200 nm, and 200 pixels of the CCD array detector are used analytically; all of them are read out individually and simultaneously, which means that the equipment works with 200 independent detectors, which opens a wide variety of new features.

5.1. Wavelength as a third dimension

First of all, the CCD array detector adds the wavelength as a new dimension to the conventional measurement of the absorbance (for steady-state signals) or absorbance over time (for transient signals). This means we can obtain a three-dimensional display of absorbance over time and wavelength, which can be of great importance in method development and to detect and avoid spectral interference.[50] Another feature that was extensively treated by Heitmann *et al.*[55] is the selection of the optimum number of pixels for the purpose; due to the fact that each pixel makes its own measurement and calculation of the absorbance or integrated absorbance, the values measured by individual pixels may be added without affecting the linearity of the calibration. In many cases the best SNR is obtained when the absorbance of 3-5 pixels is added up, and in the case of multiplets with several lines of similar sensitivity, as is the case for Mn and V, the absorbance measured at several lines of the same analyte might be added up;[55] however, if required, only one pixel or side pixels at the wings of the analytical line may be used in order to reduce the sensitivity for the measurement of higher analyte concentrations. In addition, all secondary lines are available with essentially the same emission intensity for

the determination of high analyte concentrations, due to the use of a continuum radiation source. With an HCL, in contrast, secondary lines often have much lower emission intensity and therefore an inferior SNR.

If more than one analytical line of the same element reaches the detector, and if these lines have significantly different sensitivity, the analyte can be determined simultaneously at more than one line in order to extend the working range. The first attempt in this direction was made by Vale *et al.*[56] in 2004, using the two nickel lines at 232.003 and 232.138 nm (Figure 2), the sensitivity of which is about one order of magnitude different, in order to extend the working range in the determination of Ni in crude oil and to avoid additional dilution. Resano *et al.*[57] expanded this approach to the three nickel lines at 234.554, 234.663 and 234.751 nm, which resulted in a practical working range between 20 and 50,000 pg Ni.
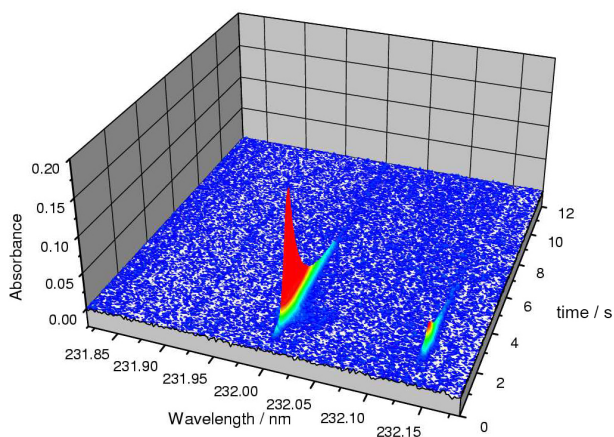

Figure 2. Time-resolved absorbance spectrum in the vicinity of the primary nickel absorption line at 232.003 nm with the secondary line at 232.137 nm (from reference 50; copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission).

5.2. Simultaneous or sequential determination using HR-CS graphite furnace AAS

Yet another feature that is available due to the use of a CCD array detector is the possibility to determine two or more elements simultaneously in cases where the lines of more than one element fall within the spectral window of the detector. The first application of this approach was reported by Dos Santos *et al.*[58] in 2009, determining simultaneously Cd at 228.802 nm and Fe at 228.726 nm, using two different atomization temperatures within the same temperature program. Table 1 shows examples where this possibility was applied successfully for simultaneous determinations using graphite furnace (GF) atomization. Resano *et al.*[57] reported the simultaneous determination of three elements in oyster tissue, and they also investigated the possibility to use an

internal standard by simultaneous determination of two elements. The same authors also proposed the sequential determination of up to three analytes of different volatility from one sample injection, using three different atomization temperatures and changing the wavelength in between the atomization cycles.[57] Duarte *et al.*[67] used the same technique for the sequential determination of Cd and Cr in biomass samples and their ashes. Resano *et al.*[68] recently published a review article about the simultaneous or sequential monitoring of multiple lines in HR-CS AAS. Obviously, the number of examples in Table 1 is not very great, mostly because of the relatively small spectral range that reaches the detector for a simultaneous determination and the also relatively small number of elements that can be determined sequentially using different atomization temperatures. Nevertheless, the applicability for some special cases has been demonstrated, but the general application for a greater number of elements has to wait until real simultaneous multi-element instrumentation becomes available.

5.3. Fast sequential determination using HR-CS flame AAS

The situation is different in the case of flame AAS, where a fast sequential determination of several analytes, and also the use of the reference-element technique (internal standard) were already proposed at the beginning of this century using conventional equipment with four HCL.[69] However, the use of line sources for this approach was shown to be a serious limitation, as in most practical applications only two elements were determined,[70-74] or one analyte and an internal standard;[75,76] however not more than three[77,78] or four analytes[79,80] although theoretically more elements could be determined using multi-element HCL.

In contrast, an unlimited number of analytes is available for fast sequential determination using high-resolution continuum source flame atomic absorption spectrometers (HR-CS F AAS), as the continuum source emits all wavelengths, and only a change of the wavelength is necessary to go from one analyte to the next. This obviously also includes the possibility of selecting more than one line *per* analyte for elements with a wide concentration range in order to extend the linear working range and to select the appropriate pixels to further adjust the conditions for a specific application. In addition, the software can change flame composition, stoichiometry, and burner height to previously optimized conditions within about a second. This makes possible to determine each analyte under optimized conditions, which is clearly preferable to a simultaneous determination under compromised conditions.

Table 1. Simultaneous or sequential determination (from the same sample aliquot) of two or more analytes using HR-CS GF AAS

Elements	Wavelengths / nm	Figures of merit	Matrix	Comments	Reference
Cd + Fe	228.802 (Cd) 228.726 (Fe)	Linear range: 3-70 pg Cd 2.6-40 ng Fe	Grain products	Direct solid sample analysis	58
Cr + Fe	357.868 (Cr) 358.120 (Fe)	LOQ 4 µg kg^{-1} 2 mg kg^{-1}	Crude oil	–	59
Cd + Fe	228.802 (Cd) 228.726 (Fe)	Linear range: 10-70 pg Cd 10-60 ng Fe, 0.2-4 µg Fe	Bean and soil samples	Direct solid sample analysis	60
Co + V	240.725 (Co) 240.674 (V)	LOQ 28 µg kg^{-1} 4.2 mg kg^{-1}	Crude oil	–	61
Cd + Fe	228.802 (Cd) 228.726 (Fe)	LOD 30 ng g^{-1} 90 µg g^{-1}	Sewage sludge	Slurry sampling	62
Ni + V	305.432 (Ni) 305.633 (V)	LOQ 1 mg kg^{-1} 0.3 mg kg^{-1}	Crude oil	–	63
Ag + Ni	338.289 (Ag) 338.057 (Ni)[a]	–	Aqueous standards	Internal standard	57
Ni + Co	231.096 (Ni) 231.136 (Co)[a]	–	Urine, blood	Internal standard	57
Fe + Pt	248.814 (Fe) 248.717 (Pt)[a]	–	Aqueous standards	Internal standard	64
Ni + Fe + Co	352.454 (Ni) 352.604 (Fe) 352.617 (Fe) 352.685 (Co)	m_0 = 30 pg m_0 = 3 ng m_0 = 27 ng m_0 = 75 pg	Oyster tissue	Direct solid sample analysis	57
Cd + Ni	228.802 (Cd) 228.998 (Ni)	–	White cabbage	Direct solid sample analysis	57
Mo + Ti	319.397 (Mo) 319.200 (Ti)	LOD 1.5 µg L^{-1} LOD 6.5 µg L^{-1}	Urine on filter paper	Direct solid sample analysis	65
Co + Fe + Ni + Pb	283.393 (Co) 283.443 (Co) 283.245 (Fe) 283.455 (Ni) 283.306 (Pb)	LOD 86 ng LOD 440 ng LOD 6 ng LOD 65 ng LOD 23 pg	Carbon nanotubes	Direct solid sample analysis	66
Cd + Ni	228.802 (Cd) 234.554 (Ni)	–	White cabbage	Sequential atomization	57
Hg + Zn + Cr	253.652 (Hg) 307.590 (Zn) 357.869 (Cr)	–	Aqueous standards	Sequential atomization	57
Cd + Cr	228.802 (Cd) 357.896 (Cr) 428.972 (Cr)	LOD 1.1 µg kg^{-1} LOD 21 µg kg^{-1} LOD 90 µg kg^{-1}	Biomass samples	Sequential atomization	67

[a]Used as internal standard. LOQ: limit of quantification; LOD: limit of detection.

Although there are some publications where only two elements were determined, such as Ca and Mg in dairy products,[81] or Pb and Sb in pewter alloy cups,[82] there are also investigations that include many more elements. Amorim Filho *et al.*[83] determined seven elements in lubricating oil, investigating different sample preparation procedures. De Oliveira *et al.*[84] also determined seven elements in plant leaves for foliar diagnosis of the nutritional status. They used the main analytical lines for copper, iron, manganese and zinc and secondary lines for calcium, magnesium and zinc. The authors also investigated side-pixel registration

to reduce the sensitivity and extend the linear working range for the determination of magnesium. Frentiu *et al.*[85] determined eight elements in soil samples and validated the fast sequential analysis for routine application. De Oliveira *et al.*[86] even determined 11 elements in plant leaves, using side pixel registration for elements that were present at high concentration. Borges Ferreira *et al.*[87] determined potassium and phosphorus in liquid fertilizers and phosphate rock using side pixel registration for K and both, atomic and molecular (as PO) absorption for the determination of phosphorus at several wavelengths.

Bechlin *et al.*[88] determined boron, phosphorus (as PO) and sulfur (as CS) in medical plants, investigating the summation of the absorbance of several lines in order to improve the limits of detection. Virgilio *et al.*[89] investigated several lines of the CS and the HS molecules for the determination of sulfur in fungicides and sulfate-based fertilizers. Matusiewicz and Krawczyk[90] determined eight hydride-forming elements in a variety of certified reference materials (CRM) and real samples using hydride generation-atom trapping combined with HR-CS F AAS using solution and slurry sampling. All papers published up to date on the fast sequential determination of more than one element using HR-CS FAAS are summarized in Table 2.

Another approach, which is also based on the fast sequential determination of more than one element, is the reference element technique, which is also called the internal standard technique. Although this technique should

Table 2. Fast sequential determination of several analytes using HR-CS flame AAS

Analyte	Wavelength / nm	LOD	Sample	Comments	Reference
Cu	324.754	5.4 µg L⁻¹	Soil extracts	Fast sequential; side pixel registration	95
Fe	248.325	147 µg L⁻¹			
Fe	252.744	55 µg L⁻¹			
Mn	279.482	3.0 µg L⁻¹			
Zn	213.875	4.5 µg L⁻¹			
Cu	324.754	4 ng g⁻¹	Lubricating oil	Fast sequential	83
Cr	357.869	23 ng g⁻¹			
Fe	248.327	7.4 ng g⁻¹			
Ni	232.003	5 ng g⁻¹			
Pb	217.001	15 ng g⁻¹			
Sb	217.581	51 ng g⁻¹			
Zn	213.857	3 ng g⁻¹			
Ca	239.856	0.6 mg L⁻¹	Sugarcane and CRM leaves	Fast sequential; side pixel registration	84
Cu	324.754	7.7 µg L⁻¹			
Fe	248.327	7.7 µg L⁻¹			
K	404.414	0.4 mg L⁻¹			
Mg	202.582	0.1 mg L⁻¹			
Mn	279.482	1.5 µg L⁻¹			
Zn	213.857	5.9 µg L⁻¹			
Al	309.271	250 ng g⁻¹	Lubricating oil	Fast sequential; different sample preparation	96
Ba	553.548	10 ng g⁻¹			
Mo	313.259	40 ng g⁻¹			
Si	251.611	40 ng g⁻¹			
V	318.398	22 ng g⁻¹			
B	249.773	1 µg g⁻¹	Sugarcane, orange tree and CRM leaves	Fast sequential; side pixel registration	86
Ca	239.856	0.15 mg g⁻¹			
Cu	324.754	0.58 µg g⁻¹			
Fe	248.327	1.6 µg g⁻¹			
K	404.414	0.12 mg g⁻¹			
Mg	202.588	48 µg g⁻¹			
Mn	279.482	0.096 µg g⁻¹			
Mo	313.259	0.016 µg g⁻¹			
P	213.618	0.14 mg g⁻¹			
S (as CS)	258.055	0.11 mg g⁻¹			
Zn	213.857	0.66 µg g⁻¹			
K	404.422	0.2 mg L⁻¹	Liquid fertilizers, phosphate rock	Fast sequential; side pixel registration for K; atomic and molecular absorption	87
P	213.618	55 mg L⁻¹			
P (as PO)	246.400	20 mg L⁻¹			
	247.620	17 mg L⁻¹			
	247.780	12 mg L⁻¹			
	324.616	18 mg L⁻¹			
	327.040	20 mg L⁻¹			
Cu	324.754	0.12 mg kg⁻¹	Vegetable oils	Fast sequential; micro-emulsion	97
Fe	248.327	0.62 mg kg⁻¹			
Ni	232.003	0.58 mg kg⁻¹			
Zn	213.857	0.12 mg kg⁻¹			

Table 2. continuation

Analyte	Wavelength / nm	LOD	Sample	Comments	Reference
B	249.773	0.5 mg L^{-1}	Medicinal plants	Fast sequential;	88
	249.677	2.9 mg L^{-1}		Summation of absorbance	
P (as PO)	246.400	28 mg L^{-1}			
	247.620	14 mg L^{-1}			
	247.780	49 mg L^{-1}			
S (as CS)	257.595	35 mg L^{-1}			
	257.958	74 mg L^{-1}			
Pb	217.001	0.2 mg L^{-1}	Pewter cups	Fast sequential	82
Sb	212.739	5.7 mg L^{-1}			
Ag	328.068	0.18 mg kg^{-1}	Soil digests	Fast sequential; method validation	85
Cd	228.802	0.14 mg kg^{-1}			
Co	240.206	0.36 mg kg^{-1}			
Cr	357.869	0.25 mg kg^{-1}			
Cu	324.754	0.09 mg kg^{-1}			
Ni	232.003	1.0 mg kg^{-1}			
Pb	217.001	1.4 mg kg^{-1}			
Zn	213.856	0.18 mg kg^{-1}			
Pb	217.001	10 µg L^{-1}	Phosphoric acid	Co used as internal standard	91
Co	283.306	17 µg L^{-1}			
^{10}B	208.959	Not given	Steel samples	Fe and Ni used as internal standards	94
^{11}B	208.957				
Si	251.611	8.4 µg L^{-1}	Lubricant oil	W used as internal standard	92
W	255.135				
Cu	324.754	4.8 µg L^{-1}	Alcoholic beverages	Bi and Te used as internal standards	93
Bi	223.061				
Te	214.135				

CRM: certified reference material.

ideally be used determining the analyte and the reference element simultaneously, all the fast sequential approaches appear to improve the results. Raposo Junior *et al.*[91] determined lead in phosphoric acid using cobalt as an internal standard and tested various elements as internal standard for the determination of Si in lubricating oil; tungsten provided the best results.[92] The same authors also investigated various elements as potential internal standards for the determination of Cu in alcoholic beverages and found that Bi gave the best results.[93] Wiltsche *et al.*[94] finally tried to determine the ^{10}B/^{11}B isotope ratio in steel samples using Fe and Ni as internal standards to correct for monochromator instability. The publications about the reference-element technique are also included in Table 2.

5.4. Background correction in HR-CS AAS

Another outstanding feature of HR-CS AAS is its unmatched background correction (BC) capability, which is also based on the use of a linear CCD array detector instead of a photomultiplier tube or a solid-state detector in LS AAS, which are integrating over the spectral range transmitted by the exit slit. The first system for automatic BC in LS AAS, proposed by Koirtyohann and

Pickett,[98] used a continuum source, usually a deuterium lamp, to measure the background absorption, which is then subtracted from the total absorption measured with the HCL. By definition, this BC works only when the background is uniform within the spectral interval transmitted by the exit slit of the monochromator, but it is used successfully even nowadays, particularly in flame AAS. Another BC system, which is based on the high-current pulsing of HCL, was introduced by Smith and Hieftje;[99] as the background is measured on both sides of the analytical line, it is also limited to background that is continuous within the measurement range. In addition, this technique can only be used for flame AAS, as the HCL needs a relaxation time after a high-current pulse, so that the measurement frequency is too low for the transient signals of GF AAS. The most successful technique to correct for background absorption in LS GF AAS is Zeeman-effect BC with an alternating magnetic field at the graphite tube atomizer.[100] This technique was improved significantly over the past decades with a variety of new features and can nowadays be considered mature.[101] Nevertheless, there are still two limitations that might affect the accuracy of this BC technique: firstly, when the background is due to a near-by atomic line or a molecular band with rotational fine

structure, and the background without and with a magnetic field is not the same, the correction is erroneous, as was shown by Heitmann *et al.*[42] for the PO molecular absorption in the vicinity of the Cd resonance line. Secondly, when the background signal changes very rapidly with time, artifacts might be observed, as the measurements of total absorption (without magnetic field) and background absorption (with magnetic field) are inevitably sequential. Independent of that, a magnet at the atomization unit makes the whole system complex and expensive.

5.4.1. Correction for continuous background

In HR-CS AAS, in contrast, the software of the instrument selects automatically (or the operator might select manually) correction pixels on both sides of the analytical line, which do not show any absorption lines. Any increase or decrease of the radiation intensity that is the same for all correction pixels will then be corrected automatically to the baseline. This includes any short-term change in the emission intensity of the radiation source (flicker noise), as well as any background absorption that is continuous within the spectral window reaching the CCD detector. This means that the signal output is already corrected for lamp noise and any continuous background, i.e., with an extremely low noise level, as is shown in Figures 3a and 3b. This is also in contrast to LS AAS, where any of the BC systems has a significant contribution to the baseline noise, which will increase at least by a factor of two or even much more, and will influence precision, LOD and the limit of quantification (LOQ).

5.4.2. Least squares background correction

What remains after this automatic correction for continuous background is the atomic absorption of the analyte and of concomitants if they have absorption lines within the spectral range of the detector. There also remains the absorption spectrum of any diatomic molecule that has an absorption band with rotational fine structure within the spectral range of the analyte absorption.[50] All these absorption phenomena are displayed as a 3D image by the software, which makes it very easy to recognize potential spectral interference and to correct for it. Firstly, any concomitant absorption that does not coincide with the analyte absorption in wavelength and/or in time does not cause any problem due to the high resolution of the double monochromator and does not need any corrective action. Only in the rare case of a direct or partial overlap of the concomitant absorption with the analyte line, further measures have to be taken. The instrument software offers in this case the so-called least-squares background correction (LSBC) using reference spectra.[50]
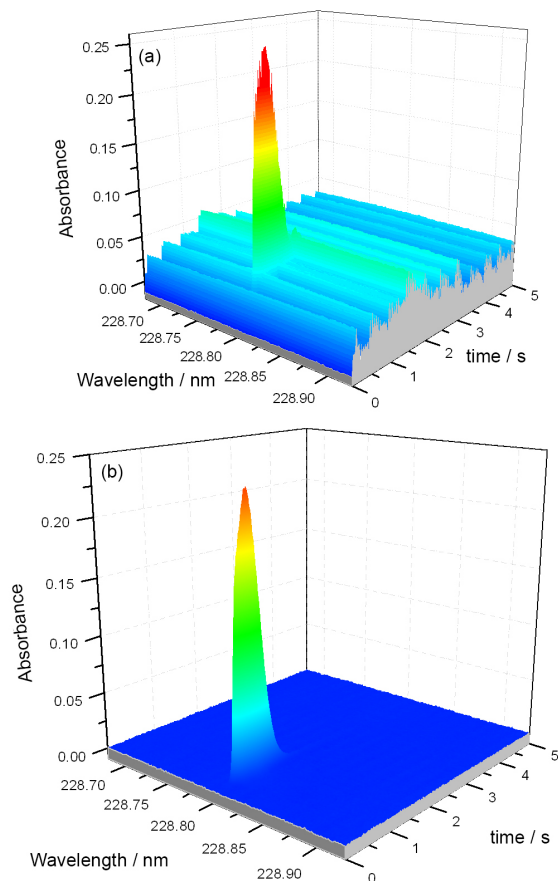

Figure 3. Time-resolved absorbance spectrum for cadmium in a fertilizer sample in the vicinity of the primary resonance line at 228.802 nm; a) without background correction; b) with automatic correction for continuous background absorption (from reference 102; reproduced with permission from Elsevier).

A fundamental requirement for the correction of fine-structured background via reference spectra is that the spectrometer is equipped with an accurate mechanism for wavelength stabilization. This feature is included in all commercial instruments, using the lines of an internal neon lamp, which fixes the absorption line with an accuracy of a few percent of a pixel, i.e., less than 0.1 pm. In addition, the reference absorbance spectra ($A_{ref,i}^{pixel}$) of the number i of molecules causing fine-structured background at the analyte wavelength position must be known (usually it is not more than one or two). These reference spectra are then used as independent linear functions in a least-squares fitting algorithm and fitted to each absorbance spectrum. The individual absorbance spectra corrected for fine-structured background are calculated as follows:

$$A_{corr,scan}^{pixel} = A_{scan}^{pixel} - \sum_i a_{scan,i} A_{ref,i}^{pixel} \tag{1}$$

The molecule correction factors $a_{scan,i}$, which are a measure of the strength of the different reference

absorbance spectra for the corresponding scan, are obtained by omission of the pixels at the analyte wavelength position, since the actual analyte absorption must not influence the background correction procedure. In practice, this correction procedure is much simpler than it sounds, as there are only a few diatomic molecules that are stable at the temperatures used for atomization, such as PO, NO, SiO, CS, and the correction is done automatically within a few seconds.

This LSBC can be used with flame and with graphite furnace atomization. A typical example for an application of LSBC with a flame atomizer is shown in Figures 4a and 4b for the determination of Bi at 306.772 nm using an air-acetylene flame.[50] Any flame used in AAS exhibits the spectrum of the OH radical due to the reaction of the fuel gas (acetylene, hydrogen) with the oxidant (air, N_2O). As the OH spectrum is produced equally for the sample solution and the calibration and blank solutions, there will be no systematic error due to that; however, as the production of the OH radical in a flame is subject to fluctuations, it contributes significantly to the baseline noise, as shown in Figure 4a. If an analyte has an absorption line in the vicinity of the OH absorption spectrum, this will significantly influence precision, LOD and quantification. It is sufficient to record and store the absorption spectrum of the pure flame within the spectral range of interest and subtract it from the sample spectrum using LSBC to arrive at an essentially noise-free baseline, as shown in Figure 4b. The same thing can obviously be done when the interfering molecular spectrum is due to a matrix component; the only difference is that in this case the origin of the interference has to be found, which is facilitated by using the 'Line Identification' tool in the software, and a pure reference spectrum be generated for correction.

Another application of LSBC is to correct for direct line overlap, such as that of a secondary iron line at 213.859 nm with the main resonance line of zinc at 213.856 nm.[50,103] In case the interfering element (in this case iron) has another absorption line within the spectral window that reaches the detector array (e.g., the iron line at 213.970 nm), firstly, the sensitivity ratio between the two lines has to be determined. Then the absorbance is measured at the 213.856-nm Zn line and at the 213.856-nm Fe line, and finally the proportional absorbance calculated from the ratio between the two iron lines is subtracted from the absorbance measured at the Zn line; obviously, all these calculations are again carried out automatically by the software of the computer.

In HR-CS GF AAS, LSBC is mostly used to correct for the absorption of di-atomic molecules, such as NO, PO, SiO, etc., with a rotational fine structure that coincides with the absorption lines of the analyte. Molecules, like atoms,
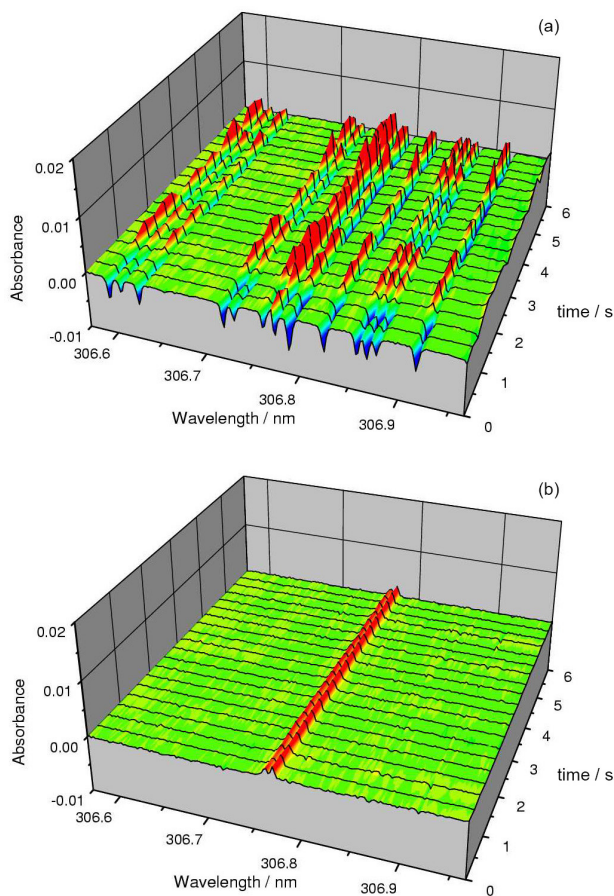

Figure 4. Influence of the OH molecular absorption in an air/acetylene flame on the determination of bismuth in the vicinity of the 306.772 nm absorption line; aqueous standard of 500 µg L^{-1} Bi; (a) without correction; (b) with LSBC for the OH absorption spectrum (from reference 50; copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission).

can absorb radiation in the UV and visible range of the spectrum, which results in a transition of an electron from the outer shell of an atom to an excited state. The major difference compared to atomic spectroscopy, where such a transition results in a single narrow absorption line, is that such a transition is accompanied by induced vibrational and rotational transitions, resulting in broad band spectra instead of line spectra. The only exceptions to this are di-atomic molecules in the gaseous state, where the rotational fine-structure can be resolved under normal analytical conditions by a high-resolution monochromator. Greater molecules usually cannot exist at the temperatures in flames and furnaces, and the few tri-atomic molecules that have been observed have such a great number of rotational lines that they cannot be resolved anymore and appear as a band structure as in UV-Vis spectrometry.

Table 3 gives an overview of publications where LSBC was used successfully in HR-CS FAAS and GF AAS. There are not too many examples in the literature for the

Table 3. Use of least-squares background correction to correct for molecular absorption with fine structure or direct line coincidence with atomic lines of concomitants

Atomizer	Analyte	Wavelength / nm	Interfering species	Sample	Comments	Reference
Flame	Pb	283.306	OH	Aqueous standard	–	50
	Bi	306.772	OH	Aqueous standard	–	50
	Zn	213.856	Fe	Iron and steel	Direct line coincidence	50,103
	Zn	213.856	Cu	High-purity copper	Direct line coincidence	50
GF	As	193.696	NaCl, PO	Urine	–	104
	Se	196.026	NO, PO	Urine	–	104
	Tl	276.787	Unidentified (S-based)	Marine sediments	Direct solid sample analysis	105
	Pb	217.001	PO	Biological CRM	Direct solid sample analysis	106
	Ni	232.003, 232.138	C_2	–	Filter furnace	107
	P	213.547, 213.618	PO	–	Different correction systems and modifiers	108-110
	Al	396.152	Unidentified (sugar and Fe)	Solutions for hemodialysis	–	111
	Ag	328.068, 338.289	Sulfur-containing molecule (SO?)	Rocks and ores	Direct solid sample analysis	112
	Sb	231.147	SiO, PO	Sediments	Direct solid sample analysis	113
	Ni	232.003, 232.138	SiO	Coal, charcoal, carbon black	Direct solid sample analysis	114
	V	318.341, 318.397, 318.538	Unidentified (S-based)	Coal, charcoal, carbon black	Direct solid sample analysis	114
	Au	242.795	PO	Mouse tissue	Direct solid sample analysis	115
	AlF	227.477	Unidentified	Whole blood	–	116

application of LSBC; this is due to the fact that, in case there is no direct overlap of the molecular structures with the atomic absorption signal, there is no need to correct for it due to the high resolution of the spectrometer. In HR-CS GF AAS there is the additional possibility to separate in time the atomic and the molecular absorption using an appropriate temperature program. An example for this is shown in Figure 5. For the same reason there is for example no need to correct for the direct line overlap of iron on zinc, as the absorption signals of Zn and Fe can be separated in time.

5.5. Molecular absorption spectrometry

5.5.1. Molecular absorption spectrometry with low-resolution AAS equipment

These spectra of diatomic molecules in flames and furnaces, however, should not only be considered as interference. Already back in the 1970s, Fuwa and colleagues[117-119] in Japan began to investigate the molecular spectrum of PO in an air-acetylene flame and finally succeeded to determine phosphorus at 246 nm with an atomic absorption spectrometer using a deuterium lamp
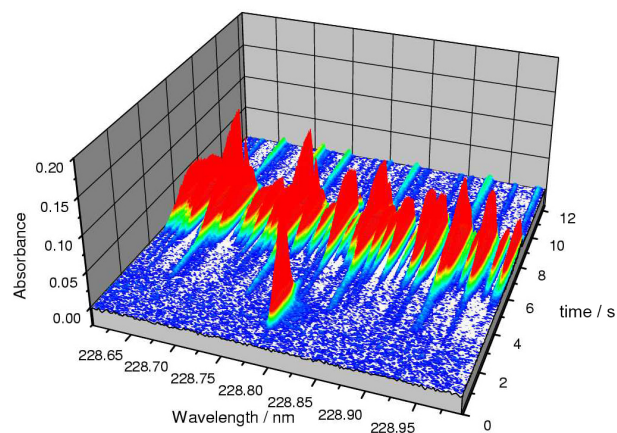

Figure 5. Time-resolved absorbance spectrum for cadmium in SARM-20 coal CRM in the vicinity of 228.802 nm using direct solid sample analysis with Ir as permanent chemical modifier (from reference 50; copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission).

and a nitrous oxide-acetylene flame. Soon after, Dittrich[120] in Germany started to investigate carefully the spectra of gallium and indium halides for the determination of halogens in a graphite furnace, using hydrogen HCL and a dual-channel spectrometer. Dittrich also published two review articles about the subject,[121,122] and several

other researchers started to work in the same field in the 1980s and 1990s. Most of them used HCL, the lines of which coincided accidentally with the spectra of diatomic molecules, and conventional LS AAS equipment. The publications using this approach are summarized in a more recent review article;[123] however, this technique never found general acceptance and was finally abandoned in the mid 1990s, mostly because of the limitations of conventional LS AAS regarding resolution and background correction.

5.5.2. Molecular absorption spectrometry with HR-CS flame AAS equipment

This situation changed completely with the introduction of HR-CS AAS, firstly, as the spectrometer of this equipment is capable of resolving the rotational fine structure of the spectra of diatomic molecules, as is shown in Figure 6 for the CS molecule, and secondly, because, due to the use of a high-intensity continuum source, any wavelength between 190 and 900 nm is available for absorption measurements. In addition, pixels that are in the 'valleys' between the rotational lines, can be used for effective correction of background absorption. In essence there are two different situations: some molecules are forming spontaneously in flames and furnaces, such as PO or CS; if this is not the case, an appropriate molecule has to be 'synthesized' by the addition of a high concentration of a 'molecule-forming reagent' to the samples and standard solutions, similar to the addition of a chemical modifier or buffer. One condition, however, has to be met in any case: the target molecule must be thermally stable enough in order not to dissociate significantly at the temperatures that are typically used in flames and furnaces. As a rule of thumb, bond dissociation energy of > 500 kJ mol^{-1} appears to be ideal.

The research on molecular absorption spectrometry (MAS) in flames using HR-CS AAS instrumentation was pioneered by the group of Becker-Ross at ISAS, Berlin, Germany. Huang *et al.*[124,125] investigated the determination of phosphorus by molecular absorption of phosphorus monoxide (PO) in an air-acetylene flame at 324.62 nm and investigated carefully potential interferences. The addition of titanium removed signal suppression due to Ca and Mg. Huang *et al.*[126] also investigated the determination of sulfur by molecular absorption of carbon monosulfide (CS) in an air-acetylene flame at 258.056 nm; the only serious interference they found was due to high concentrations of Pb, which resulted in precipitation of PbS. The same authors also reported the determination of fluorine via the molecular absorption of the gallium fluoride (GaF) molecule at 211.248 nm,[127] and of chlorine via the molecular absorption of the indium chloride (InCl) molecule at 267.24 nm.[128] These and some more recent publications about the
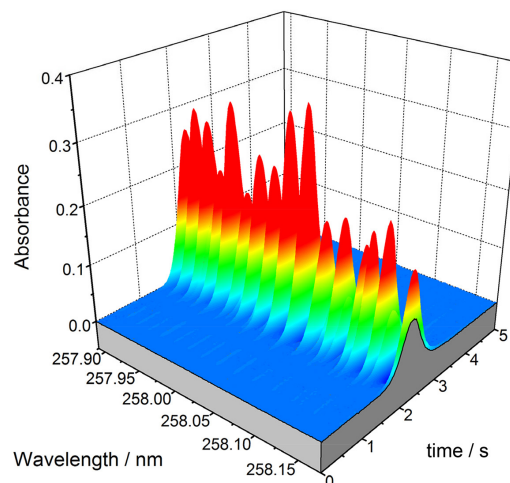

Figure 6. Time-resolved absorbance spectrum of the CS molecule in the vicinity of the absorption line at 258.033 nm obtained for NCS DC 73349 Bush Branches and Leaves CRM using direct solid sample analysis and Pd as a chemical modifier (from reference 141; reproduced with permission of The Royal Society of Chemistry).

determination of non-metals via HR-CS flame MAS are compiled in Table 4.

Another very interesting work was published by Huang *et al.*[129] using MAS for the speciation analysis of different sulfur forms, including free and total sulfur dioxide in wine. The authors, among other things, used the fact that free SO$_2$ is liberated from the sample to the vapor phase in the nebulization process, and hence transported to the flame almost quantitatively. In contrast to this, only about 5% of all the other sulfur contents reach the flame, whereas the rest goes down the drain, as is well known for burner chambers typically used in AAS. The same effect was observed by Kowalewska for the determination of sulfur in petroleum derivatives using flame MAS.[130] The major problem was that in this case there might be several different sulfur compounds of different volatility in petroleum derivatives, which might reach the flame to a different and unknown extent, which impeded quantitative determination.

5.5.3. Molecular absorption spectrometry with HR-CS GF AAS equipment

The group of Becker-Ross was also pioneering the research about the determination of non-metals via MAS in a graphite furnace (GF MAS) using HR-CS AAS equipment. Heitmann *et al.*[136] published a preliminary study about the determination of phosphorus, sulfur, fluorine and chlorine using GF MAS. Similar to flame MAS, phosphorus monoxide, PO, is forming spontaneously also in the graphite furnace and does not need a chemical modifier. Heitmann *et al.* reported an LOD of 0.9 ng P at the 246.40 nm band head. For the determination of sulfur,

Table 4. Determination of non-metals via molecular absorption in flames

Analyte	Molecule	Wavelength / nm	Flame	LOD	Sample	Reference
P	PO	324.62	Air-C_2H_2	1.3 mg L^{-1}	CRM	124
	PO	324.62	Air-C_2H_2	–	Superphosphate, pine needles CRM	125
	PO	249.337	Air-C_2H_2	13.7 mg L^{-1}	Plant material	131
S	CS	258.056	Air-C_2H_2	2.4 mg L^{-1}	Wine	132
	CS	258.056	Air-C_2H_2	2.4 mg L^{-1}	Cast iron CRM	126
	CS	258.056	Air-C_2H_2	1.8 mg L^{-1}	Sulfur forms in wine	129
	CS	258.056	Air-C_2H_2	18 mg kg^{-1}	Petroleum products	130
	CS	257.595	Air-C_2H_2	12.6 mg L^{-1}	Fertilizer, fungicide	133
	CS	358.056	Air-C_2H_2	0.01% m/m	Coal	134
	CS	257.595, 257.958	Air-C_2H_2	30.5 mg L^{-1}	Plant material	131
F	GaF	211.248	Air-C_2H_2	1 mg L^{-1}	Superphosphate CRM	127
	AlF	227.461	Air-C_2H_2	5.5 mg L^{-1}	Toothpaste	135
Cl	InCl	267.24	Air-C_2H_2	3 mg L^{-1}	Sediment CRM	128

the authors found it necessary to coat the platform with Zr and to introduce methane gas during the pyrolysis stage as an alternate gas in order to promote the formation of the CS molecule. Like in flame MAS, the authors used the absorption of the GaF molecule for the determination of fluorine, but they preferred the AlCl molecule to determine chlorine. In all of these cases it was found necessary to coat the platform with Zr as a permanent modifier in order to obtain reliable results.

Soon after, Huang *et al.*[137] reported the determination of bromine using the molecular absorption of AlBr at 278.914 nm and of CaBr at 625.315 nm; each of the lines had advantages and disadvantages regarding interferences from matrix constituents. The latter one showed interferences due to HF, and high Na and K concentrations, which were not observed with the former one. However, interferences due to phosphoric and sulfuric acid were observed for AlBr, but not for CaBr. The same authors also reported the determination of iodine via the spectrum of barium mono-iodide, BaI, at 538.308 nm;[139] however, they found significant interference from chloride, fluoride, iron, potassium and sodium, which might complicate the determination of iodine in real samples. Finally, Huang *et al.*[139] also reported the determination of nitrate using the NO absorption line at 215.360 nm; however, the authors also found strong interference from several acids and metal ions, which they tried to overcome by using a pyrolysis temperature of only 150 °C. Some more details about these publications are given in Tables 5 and 6.

Phosphorus is kind of a special case, as this analyte can be determined both by AAS using the non-resonance doublet at 213.547/213.618 nm, and by MAS using one of the rotational lines of PO, such as the band heads at

234.62 or 246.40 nm. Lepri *et al.*[108] found that without the addition of any chemical modifier, PO is formed almost exclusively in the vaporization stage; however, the addition of a chemical modifier, such as Pd, favors the formation of atomic P in a graphite furnace and inhibits the formation of PO almost completely. They therefore concluded that the formation of atoms is easier to control than the formation of PO molecules. Resano *et al.*[140] made a careful comparison between HR-CS GF AAS and HR-CS GF MAS for the determination of phosphorus in biological CRM using direct solid sample analysis. For AAS it was necessary to use W as a permanent chemical modifier together with palladium and ascorbic acid in solution, and an atomization temperature of 2650 °C. For MAS it was sufficient to use W as a permanent modifier and a vaporization temperature of only 1900 °C; however, the LOD with AAS was 4.9 ng P, whereas that for MAS was 21 ng, summing nine PO lines between 213.508 and 213.646 nm. In addition, some spectral interference due to NO was observed; hence, the decision which analytical technique should be preferred might depend on the analytical task.

Sulfur cannot be determined by AAS, as all its absorption lines are below 190 nm, a spectral range not accessible with this technique; hence, MAS adds one more analyte to the list of elements that can be determined using HR-CS GF AAS equipment. Most authors used the CS molecule, proposed by Huang *et al.*[126,132] for flame MAS, and by Heitmann *et al.*[136] for GF MAS, although slightly different wavelengths have been chosen by some of the authors in order to avoid minor spectral interference, as shown in Table 5.[141-143] Resano *et al.*[142] also investigated the sum of six lines of the CS spectrum and succeeded

Table 5. Determination of sulfur using HR-CS GF MAS

Molecule	Wavelength / nm	Modifier	LOD	Sample	Preparation	Reference
CS	258.056	Zr + Ca + CH$_4$	2.3 ng	Spinach, peach leaves CRM	Digestion	136
CS	258.033	W + Pd	15 ng	Biological CRM	Direct solid sample analysis	141
CS	257.958 Sum of 6 lines	Ru and Pd nanoparticles	9 ng 3 ng	Steel, coke, PE, biological CRM	Direct solid sample analysis	142
CS	258.033	Ru	30 ng	Coal, coal CRM	Direct solid sample analysis	143
CS	258.056	Ir + Pd	3.5 ng	Food, food CRM	Direct solid sample analysis	144
CS	258.056	Pd + Mg	14 ng	Petroleum products	Dilution in xylene	130
CS	257.592	None	0.15 mg L^{-1}	Coal and ash	Slurry sampling	145
SnS	271.578	Zr	0.16 ng	Water	Direct analysis	146

PE: Polyethylene

to improve the LOD by a factor of 3. Kowalewska,[130] who found it almost impossible to determine sulfur in petroleum products using flame MAS because of the very much different volatility of the various sulfur compounds, succeeded to determine sulfur at least in the heavier crude oils using GF MAS.

The formation of the CS molecule in HR-CS GF MAS is considered a spontaneous reaction, as there appears to be sufficient carbon available in the graphite tube atomizer. Nevertheless, it was already observed by Heitmann *et al.*[136] that the tube or platform surface has to be coated with a carbide-forming element in order to avoid direct contact between the sample and the graphite, a practice that was also used by all other authors (see Table 5). The reason for this is to avoid a competitive reaction between sulfur and carbon that results in the formation of the highly volatile carbon disulfide, CS$_2$, which is actually produced on a large scale using this reaction.[141] Hence, the CS molecule might be a good choice for the determination of sulfur in case the sample contains sufficient carbon, such as biological samples, petroleum products or coal (see Table 5); however, it might not form spontaneously in other cases. Baumbach *et al.*[146] investigated therefore the SnS molecule, which has already been proposed by Parvinen and Lajunen in the 1990s for the determination of sulfur using LS AAS.[147] It might well be that this molecule is better suited for the determination of sulfur in samples that do not contain sufficient carbon for the formation of CS, such as digested samples.

Heitmann *et al.*[136] used the rotational fine structure of the GaF molecule to determine fluorine in zinc ore and single cell protein CRM after digestion using the analyte addition technique to control potential interference. They coated the graphite platform with Zr and used Mg as an additional chemical modifier. Gleisner *et al.*[148] also using GaF as the target molecule, investigated various additional modifiers

in order to improve sensitivity, and succeeded to determine fluorine in natural and drinking water samples using aqueous solutions for calibration. Later, Gleisner *et al.*[149] reported the determination of total and soluble fluorine in toothpaste using slurry sampling and aqueous standards for calibration. The results were in good agreement with a headspace gas chromatographic method with mass spectrometric detection. Morés *et al.*[150] investigated the CaF molecule for the determination of fluorine in tea after different ways of sample preparation; they found that in this case no additional modifier is required, as Ca acts as molecule forming agent and also as chemical modifier, simplifying the procedure significantly. This was confirmed by Ozbek and Akman in the determination of fluorine in milk and waste water CRM.[151] The same authors also investigated the SrF molecule for the determination of fluorine in water.[152] Bücker and Acker[153] investigated the AlF molecule for the determination of fluorine in process etching solutions, using barium as an additional chemical modifier. Krüger *et al.*[154] reported an interesting application determining 5-fluorouracil in cancer cells using GaF as the target molecule and calcium as an additional chemical modifier. Ozbek and Akman[155] investigated the absorption of the SrF molecule at 651.187 nm. Some more details about these publications are given in Table 6.

A very interesting work was published by Qin *et al.*,[156,157] in which they described an off-line coupling of reverse-phase high-performance liquid chromatography (HPLC) with HR-CS GF MAS for the speciation analysis of organo-fluorine compounds. Fractions of the eluents of the isocratic separation were collected and placed in the autosampler of the HR-CS AAS equipment for the determination of the fluorine content, using the absorption line of the GaF molecule at 211.248 nm. Several modifiers, including Zr, Pd, Mg and sodium acetate, were used. The

Table 6. Determination of halogens using HR-CS GF MAS

Analyte	Molecule	Wavelength / nm	Modifier	LOD	Sample	Treatment	Reference
F	GaF	211.248	Zr, Mg	9 pg	Zinc ore, single cell protein CRM	Digestion	136
	GaF	211.248	Zr, Pd, Ru, sodium acetate	5.2 pg	Water	Direct	148
	GaF	211.248	Zr, Pd, $NH_4H_2PO_4$	5.2 pg	Toothpaste	Slurry	149
	CaF	606.440	None	1.6 ng	Tea	Digestion, infusion	150
	CaF	606.440	None	260 pg	Milk, waste water CRM	Direct	151
	SrF	651.187	None	550 pg	Water	Direct	152
	AlF	227.46	Ba	145 pg	Process etching solutions	Dilution	153
	GaF	211.248	Ca	33 pg	5-Fluorouracil in cancer cells	Dilution	154
	SrF	651.187	Zr	–	Investigation of mechanisms	–	155
	GaF	211.248	Zr, Pd, Mg, sodium acetate	–	Speciation analysis of organo-fluorine compounds separated by HPLC	Dilution	156
	GaF	211.248	Zr, Pd, Mg, sodium acetate	–	Speciation analysis of organo-fluorine compounds separated by HPLC	Dilution	157
Cl	AlCl	261.42	Sr	70 pg	Rye flour	Digestion	136
	AlCl	261.418	Al, Ag, Sr	9 µg g^{-1}	Food samples	Digestion	158
Br	AlBr CaBr	278.914 625.315	None	2 ng	Salt, pharmaceutical sample	Dissolution	137
	CaBr	625.315	Zr, Pd-Mg	78 pg	Organo-bromine compounds, flame retardants	Digestion	159
	CaBr	Various	Pd	1.3-5 ng	Plastic CRM	Direct solid sample analysis	160
I	BaI	538.308	None	600 pg	Iodine pill, thyroid pill	Dissolution	138

results were compared with those obtained by HPLC electrospray ionization mass spectrometry (ESI-MS), and HR-CS GF MAS was shown to be an effective detector for fluorine speciation analysis; nevertheless, the off-line coupling might not be very suitable for routine analysis.

Besides the early paper of Heitmann *et al.*,[136] only one more paper has been published about the determination of chlorine using HR-CS GF MAS. Fechetia *et al.*[158] used an Al-Ag-Sr modifier, which was injected together with the sample solution to determine Cl in food samples. Two different sample preparation procedures were investigated: an acid digestion with nitric acid at room temperature and a digestion with Ag, HNO_3, and H_2O_2, where chlorine is precipitated as low-soluble AgCl, which is then dissolved with ammonia solution. The results obtained with the latter method were found to be in good agreement with certified values for the investigated CRM. The mixed modifier caused some spectral interference, which could, however, be easily corrected using LSBC.

The determination of bromine is hampered by the relatively low dissociation energy of its diatomic molecules, as was already observed by Huang *et al.*.[138] Only two additional papers were published on this topic. The first one is by Limburg and Einax[159] for the determination of Br

in organobromine compounds and flame retardants using the absorption line of the CaBr molecule at 625.315 nm. The authors used Zr as a permanent modifier and a Pd-Mg modifier added in solution, and they found better performance when a graphite tube without platform was used. Nevertheless, the authors found interferences due to fluoride, chloride, iodide, sulfate, aluminum and iron, which might limit the applicability of the method. Flórez and Resano[160] determined bromine in plastic material using direct solid sample analysis and aqueous standard solutions for calibration. Some additional information on the determination of halogens using HR-CS GF MAS may be found in Table 6.

The determination of iodine by HR-CS GF MAS is also hampered by the low dissociation energies of its molecules. Huang *et al.*[138] used the BaI molecule, which has the relatively highest dissociation energy of 327 kJ mol^{-1} to determine iodine in an iodine pill and a thyroid hormone pill using the analyte addition technique; however interference due to a number of concomitants was reported. No other publication about the determination of iodine has appeared up to now, most likely due to the difficulties associated with the low dissociation energy of the iodine molecules.

Huang *et al.*[139] also used the absorption line of the NO molecule at 215.360 nm to determine nitrate in different CRM using HR-CS GF MAS and Ca as a modifier. Interferences were avoided using a pyrolysis temperature of only 150 °C. Bücker and Acker[153] reported a determination of nitrate in silicon wafer etching solutions using the NO absorption at 214.803 nm and lanthanum as a modifier. Brandao *et al.*[161] proposed a different approach for the determination of nitrite using a chemical generation of NO and its determination in a non-heated quartz cell at 215.360 nm. NO was generated in 0.4 mol L^{-1} HCl with 1.5% (m/v) ascorbic acid as the reducing agent; the authors reported an LOD of 45 µg L^{-1} nitrite.

Aramendia *et al.*[116] made the surprising proposal to determine Al, which can obviously be determined directly with AAS, using the molecular absorption of AlF. The authors used NH$_4$F·HF as the molecule-forming reagent and also as the chemical modifier and monitored the line at 227.402 nm using five pixels. Spectral interference was observed in the determination of Al in blood, which could be corrected using LSBC. The method was applied to forensic drowning diagnosis analyzing blood and drowning water.

There were also two review articles published recently by Butcher[162] and Resano *et al.*[163] about molecular absorption spectrometry using high-resolution AAS equipment, which might be of interest for the reader.

5.6. Direct analysis of solid samples

The direct analysis of solid samples using AAS is as old as the technique itself, particularly when a graphite tube furnace is used for atomization.[2,164] In 1998 Kurfürst[165] published a book about this technique, and there appeared at least two review articles more recently,[166,167] describing the advantages and limitations of this technique for sample introduction and analysis, which will not be repeated here. Hence, direct solid sample analysis is not directly related to HR-CS GF AAS; however, it has been shown that HR-CS GF AAS makes direct solid sample analysis much easier and much more reliable, mostly due to the fact that the spectral environment of the analytical line can be displayed at high resolution, and due to the superior background correction capabilities.[167]

The more recent publications about direct solid sample analysis using HR-CS GF AAS or MAS are shown in Table 7. Several of these publications have been discussed before in a different context, such as the simultaneous determination of Cd and Fe in grain products[58] and in bean and soil samples,[60] the simultaneous and sequential atomization of Cd and Ni in white cabbage CRM,[57] the simultaneous determination of Co, Fe and Ni in oyster tissue CRM,[57] the simultaneous determination of Co, Fe, Ni and Pb in carbon nanotubes,[66] or the sequential atomization of Cr, Hg and Zn in aqueous standards,[57] and of Cd and Cr in biomass and ashes.[67] The analyzed materials include airborne particulate matter collected on glass fiber filters,[168,171,175] coal,[143,169,173,176] and activated charcoal and carbon black.[114] It is only natural that direct solid sample analysis was already applied equally for the determination of non-metals, such as Br in plastic materials[160] or sulfur in wide variety of samples.[141-144] Essentially, all these measurements were carried out using aqueous standard solutions for calibration, which means without spectral or non-spectral interference. This is, besides the rigorous use of the stabilized temperature platform concept in order to control non-spectral interferences,[178] due to the unsurpassed background correction capability of the HR-CS AAS instruments. An impressive example of that is shown in Figure 7 for the determination of Sb in sediment CRM.[113]

Table 7. Publications about direct solid sample analysis using HR-CS GF AAS and MAS

Analyte	Wavelength / nm	Modifier	Matrix	Calibration	Comments	Reference
Ag	328.068 338.289	None	Geological CRM	Aqueous standards for soils and sediments; solid CRM for rocks and ores	Interference due to sulfur	112
Ag	338.289	Ru permanent	Air particulate matter	Aqueous standard solutions	–	168
Br (via CaBr)	Various	Pd	Plastic materials	Aqueous standard solutions	–	160
Au	242.795	–	Mouse tissue	–	–	115
Cd	228.802	Ir permanent	Coal	Aqueous standard solutions	–	169
Cd + Cr	228.802 (Cd) 357.896 (Cr) 428.972 (Cr)	None	Biomass samples	–	Sequential atomization	67
Cd + Fe	228.802 (Cd) 228.726 (Fe)	–	Grain products	Aqueous standard solutions	Simultaneous determination	58
Cd + Fe	228.802 (Cd) 228.726 (Fe)	–	Bean and soil samples	Aqueous standard solutions	Simultaneous determination	60

Table 7. continuation

| Analyte	Wavelength / nm	Modifier	Matrix	Calibration	Comments	Reference
Cd + Ni	228.802 (Cd) 228.998 (Ni)	–	White cabbage	–	Simultaneous determination	57
Cd + Ni	228.802 (Cd) 234.554 (Ni)	–	White cabbage	–	Sequential atomization	57
Co	240.725	None	Biological material	Aqueous standard solutions	Comparison with alkaline solubilization	170
Co + Fe +Ni	352.685 (Co) 352.604 (Fe) 352.617 (Fe) 352.454 (Ni)	–	Oyster tissue	–	Simultaneous determination	57
Co + Fe + Ni + Pb	283.393 (Co) 383.443 (Co) 383.245 (Fe) 383.455 (Ni) 383.306 (Pb)	–	Carbon nanotubes	–	Simultaneous determination	66
Cr, Cu, Fe, Mn, Mo, Ni, V	357.869 (Cr) 324.754 (Cu) 344.099 (Fe) 344.388 (Fe) 403.076 (Mn) 313.259 (Mo) 232.003 (Ni) 232.138 (Ni) 318.540 (V)	None	Activated charcoal and carbon black	Aqueous standard solutions (for Cu, Fe, Mo, and Ni); NIST SRM 1635 (for Cr, Mn and V)	–	114
Cr + Hg + Zn	357.869 (Cr) 253.652 (Hg) 307.590 (Zn)	–	Aqueous standards	–	Sequential atomization	57
Cu, Mo, Sb	324.754 (Cu) 216.509 (Cu) 313.259 (Mo) 212.739 (Sb)	Ru permanent (for Sb only)	Air particulate matter	Aqueous standard solutions	Comparison with acid digestion	171
Hg	253.652	None	Biological materials	Aqueous standard solutions stabilized with $KMnO_4$	–	172
Hg	253.652	None	Air particulate matter	Aqueous standard solutions stabilized with $KMnO_4$	–	173
Hg	253.652	$KMnO_4$	Polymers	Aqueous standard solutions	–	174
Mo + Ti	319.397 (Mo) 319.200 (Ti)	None	Urine on filter paper		Simultaneous determination	65
Pb	217.001	Ru permanent	Biological materials	Aqueous standard solutions	Comparison with calibration against CRM	106
Pb	217.001	None	Coal CRM	Aqueous standard solutions	–	175
S (via CS)	258.033	W + Pd	Biological CRM	Aqueous standard solutions of thiourea	–	141
S (via CS)	257.958 Sum of 6 lines	Ru + Pd nanoparticles	Steel, PE, biological CRM, coke	Aqueous standard solutions	–	142
S (via CS)	258.033	Ru	Coal and coal CRM	Aqueous standard solutions of L-cysteine	–	143
S (via CS)	258.056	Ir + Pd	Food and food CRM		–	144
Sb	231.147	Ir permanent	Sediment CRM	Aqueous standard solutions	Least squares background correction	112
Sb	212.739	Ru permanent	Airborne particulate matter	Aqueous standard solutions	–	176
Tl	276.787	None	Coal and coal CRM	Aqueous standard solutions	Identical results without and with Ru permanent or Pd modifier	177
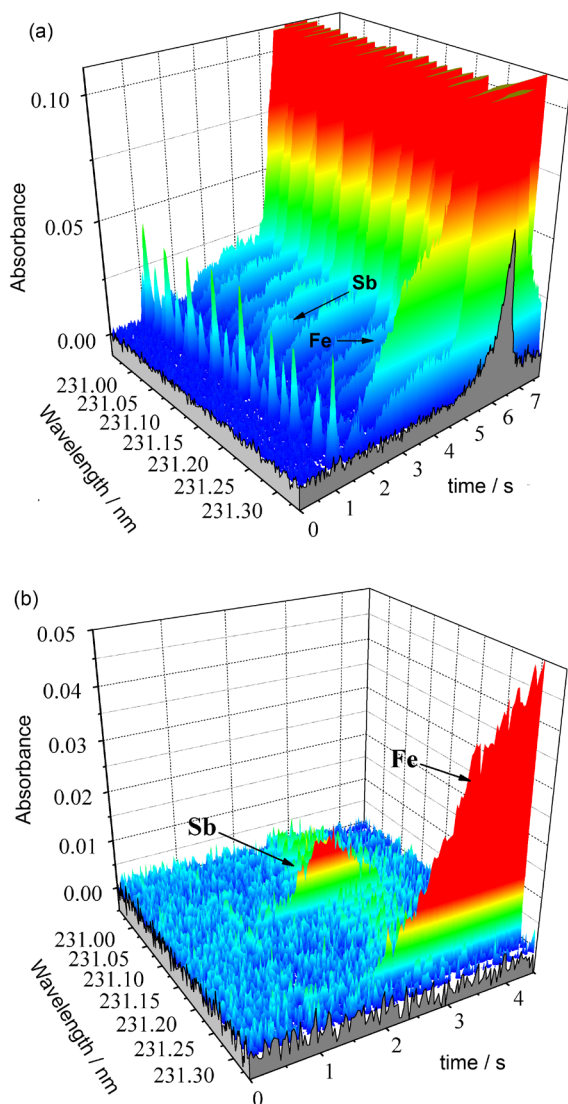
Figure 7. Time-resolved absorbance spectra recorded for NIST SRM 8704 (Buffalo River sediment) in the vicinity of the antimony line at 231.147 nm using direct solid sample analysis and Ir as permanent chemical modifier; a) after automatic correction for continuous background; b) after correction for discontinuous background absorption using the reference spectra of SiO and PO for LSBC (from reference 113; reproduced with permission from Elsevier).

6. Future Outlook

Every user of a new kind of equipment will have a wish list of what could be improved, after having used the instrument for some time. We do not want to go into these details, which can be solved by the engineers when they design a second-generation line of instruments or even by updating the software. The most frequently asked question is undoubtedly: when can we expect an HR-CS AAS instrument with truly simultaneous determination of all or at least of selected elements? This is actually not an important issue for HR-CS flame AAS, as for this technique the fast sequential determination using

optimized conditions for each analyte appears to be the best solution compared to a simultaneous determination using compromised conditions. The question is much more important for HR-CS GF AAS, as with this technique the frequency of determinations is much slower, so that the gain in analytical throughput would be much more important. Obviously, also with this technique, not all elements can be determined under the same conditions, i.e., pyrolysis and atomization temperature, without serious compromises; however, it has already been demonstrated that certain groups of elements could be determined simultaneously or with sequential atomization from the same aliquot with significant advantage regarding the time of analysis.

We would like to close this outlook with some comments made by Becker-Ross *et al.*[179] in a review article written in 2006: "The ideal detector would be a two-dimensional array with approximately 4 megapixels, high quantum efficiency down to 190 nm, fast random access and low readout noise. Unfortunately, the many megapixel detectors used in consumer applications are neither UV sensitive, nor capable of random access. Simultaneous multi-element HR-CS AAS with adequate analytical performance would require the use of custom-designed detector, which would be prohibitively expensive at this time". We tend to agree with this statement and think that there were no dramatic changes in the overall situation; hence, we have to wait for further development in the detector technology regarding the above-mentioned requirements.

Becker-Ross *et al.*[179] continue "that there are four important items to note: (*i*) the focus on the development of sequential HR-CS AAS… (*ii*) the concentration of efforts on the background correction problem, which is the main drawback of LS AAS… (*iii*) the use (development) of an improved high-intensity hot spot arc lamp that solves the problems below 200 nm and (*iv*) the use of molecular absorption in promising new methods for the determination of non-metallic elements". All of these items are currently under investigation, and significant progress has already been achieved since 2006. It appears so as if the engineers and the researchers would have to work a few more (but hopefully not too many) years before the dream of a really simultaneous HR-CS GF AAS equipment becomes reality.

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