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This work tries to provide guidance for the development of new methods aiming at the direct analysis of solid samples or complex liquid materials with HR CS GFAAS

High-resolution continuum source graphite furnace atomic absorption spectrometry for direct analysis of solid samples and complex materials. A tutorial review.

Martín Resano,[a]* Maite Aramendía[b] and Miguel A. Belarra[a]

[a] Department of Analytical Chemistry, University of Zaragoza, Pedro Cerbuna 12, 50009 Zaragoza, Spain. E-mail: mresano@unizar.es; Tel: +34 976761634.

[b] Centro Universitario de la Defensa-Academia General Militar de Zaragoza, Carretera de Huesca s/n, 50090, Zaragoza, Spain.

Abstract

The purpose of this review is to examine the literature devoted to direct sample analysis using high-resolution continuum source atomic absorption spectrometry in a tutorial way, in an attempt to provide guidelines on the most critical issues to consider when developing a new method. The review discusses in detail the advantages and limitations of this technique, highlighting its benefits in comparison with classic line source atomic absorption spectrometry instrumentation in the context of direct analysis of solid samples, slurries and complex liquid samples, trying to establish in which situations the use of this technique can be particularly beneficial. Some of the aspects that are addressed comprise: i) the improved potential to detect and correct for spectral interferences; ii) the different options to adjust the sensitivity to the analyte content; iii) strategies to minimize matrix effects and calibrate with aqueous standard solutions; iv) possibilities to carry out multi-element determinations.

1. Introduction

As it is well-established in the scientific literature, direct analysis of solid samples offers a number of important advantages in comparison with wet chemistry approaches, resulting from the elimination of the dissolution step. Indeed, with such methodology:[1] 1) results can be obtained in a much faster way; 2) the risk of contamination is considerably reduced, as well as the risk of analyte loss; 3) sensitivity increases as samples are not diluted; 4) normally, a smaller amount of sample is required; 5) it is possible to obtain information on the distribution of the analyte that is typically lost if the sample is digested; 6) the use of corrosive or hazardous reagents is not required or, at least, it is greatly minimized, thus embracing one of the principles of Green Chemistry.[2]

Focusing on elemental analysis, there are various techniques that can provide quantitative information directly from a solid sample, such as X-ray fluorescence,[3] laser induced breakdown spectrometry,[4] inductively coupled plasma mass spectrometry when coupled to laser ablation[5] or electrothermal vaporization,[6] glow discharge with atomic emission or mass spectrometry for detection,[7] to name just a few. Among these, graphite furnace atomic absorption spectrometry (GFAAS) offers a nice array of features, because it permits analysis of all kinds of samples (powders or compact materials, both conducting or non conducting samples) with minimal to none sample preparation (e.g., no need to prepare pellets), it is cost-effective, sensitive and very often calibration can be carried out in a very straightforward way, constructing the curve with aqueous standard solutions, which is very unusual for solid sampling techniques.

In fact, GFAAS has always been considered as a suitable technique for direct analysis of complex materials. The first GFAAS experiments were actually conducted by L'vov introducing a solid sample into the furnace.[1] However, the development of solid sampling (SS) GFAAS has been relatively unusual, since the number of articles devoted to this topic is rather constant through the years (around 10 articles per year), such that the subject has neither been totally disregarded nor can be considered as well established in Analytical Chemistry, particularly outside the Academic community. This is probably because, in addition to these significant advantages, the technique shows some disadvantages as well, which will be discussed in detail in the next section. But perhaps the most relevant one is the persisting notion that it is quite complicated to develop a new method, as expertise in a number of complex issues (e.g., atomization/vaporization mechanisms) is required.

During the last decade the appearance of high-resolution continuum source atomic absorption spectrometry (HR CS AAS) instrumentation has brought new possibilities to this mature field.[8] Use of a continuum source device to perform AAS was investigated by different authors over the years,[9-13] but it was finally Becker-Ross and co-workers[14-17] who presented a device that proved sufficiently successful to be commercialized by Analytik Jena in 2003 equipped with a flame as atomizer. This device was later adapted to incorporate also a graphite furnace. This instrument is based on: (1) a high-pressure xenon short-arc lamp operating at brightness temperatures of approximately 10,000 °C, capable of providing a high intensity in the visible and (far) UV region; (2) an optical system based on an echelle monochromator dispersing radiation in two

steps (by using a prism first and an echelle grating afterwards); and (3) a linear CCD array for detection. The set-up of this instrument is shown in **Figure 1**.

This technology, which essentially adds an extra dimension (wavelength) to traditional line source (LS) AAS signals, has opened up new possibilities in this field, such as a significantly improved potential for detecting and correcting for both spectral overlaps and matrix effects,[8] which are particularly relevant when direct analysis of difficult samples is intended. Thus, it is not surprising to confirm that scientists have made use of this technological improvement to develop new applications. In fact, as shown in **Figure 2a**, most of the articles devoted to HR CS GFAAS have investigated the direct analysis of solid samples or slurries or of other complex materials (e.g., oil) that are not solids, but for which it can be beneficial to develop direct methodologies (without dilution of digestion). The number of articles on this topic is actually growing since the first article published by Welz *et al*. using slurries for sample introduction.[18] This fact is not surprising since HR CS GFAAS instrumentation became commercially available only in 2008. Thus, most research groups were able to get access to such type of device only recently. In fact, it can be clearly appreciated in **Figure 2b** that scientists in the field are abandoning the traditional LS instruments and increasingly using HR CS GFAAS for these kind of complex applications, realizing the key benefits that HR CS GFAAS provides.

However, despite of these positive trends, it can also be said that HR CS GFAAS literature is still vastly dominated by a few research groups, and very few users with no previous experience in SS GFAAS are joining the field. It is our view that there is a clear need for a review with a tutorial focus to make it easier for new users to work in this area. In fact, it is a bit surprising that despite

the various reviews dealing with HR CS GFAAS that have been published so far,[19-26] none of them has been devoted to solid sampling except for one article dating from 2007,[27] at which time only 6 articles on this subject were available.

Thus, it is the purpose of this article to review the HR CS GFAAS literature of the last decade that have focused on direct analysis of solids in a tutorial way, discussing in detail the benefits and drawbacks of the technique, highlighting the major advantages in comparison with LS instrumentation, trying to establish in which situations the use of this technique can be particularly beneficial and providing some guidelines on key issues to consider when developing a new method.

This review will cover all HR CS GFAAS articles in which direct solid sample analysis is intended, but also those in which direct (meaning no digestion or even dilution is carried out) analysis of complex liquid samples is reported, since in both cases very similar problems are encountered. The few papers published to date devoted to slurry sampling will also be included in the application section. The main differences among these sampling approaches will be also noted (e.g., slurry sampling provides flexibility for diluting the sample as required), whenever they apply.

2. Pros and cons of SS HR CS GFAAS. When does it really make sense?

The advantages deriving from using SS CS HR GFAAS have been already presented in the previous section and are displayed in **Figure 3**. These benefits are significant, but it is necessary to consider also the potential disadvantages to define the most prospective fields of applications.

In this regard, it is important to state that some of the traditional drawbacks associated with SS GFAAS can hardly be considered as such today. For

instance, introducing the sample into the graphite furnace has not always been simple, since most commercially available GFAAS instruments were designed to work with solutions or, in the best of cases, with slurries. However, nowadays there is specific instrumentation for this purpose commercially available for both LS and HR CS devices. Such instrumentation simply permits the deposition of the sample onto a graphite platform that is weighted (with precision down to 1 µg) and subsequently introduced into the graphite tube. A picture of this device is shown in **Figure 4**. There are both manual and automated versions of this instrument, which can even dispense a liquid onto the platform (e.g., a modifier solution), such that unattended operation is possible. In fact, as pointed out by Vale *et al*.[28] it may be more complicated today to work with slurries, since there is no longer a commercially available instrumentation to stabilize and dispense the suspensions, contrary to what occurred in the past. It seems like the improvements in direct solid sampling together with the improvements also experienced by digestion devices have left less room for slurries.

The other traditional problem associated with SS GFAAS was the need to look for a suitable calibration strategy. The difficulties for finding perfectly matrix-matched standards or the tediousness of using standard additions are well-known, but it is important to stress that the vast majority of articles using SS HR CS GFAAS have demonstrated that it is feasible to obtain accurate results simply by constructing the curve with aqueous standard solutions, which is of course the fastest and more straightforward approach, easy to do in any lab. This trend of using aqueous standard solutions was already obvious during the last decade even when using line source devices,[27-29] as a consequence of the increased use of chemical modifiers and the proper optimization of the

temperature program. Therefore, it is not surprising to check that this case is even more pronounced when HR CS GFAAS is deployed, since the latter technique provides a superior performance in terms of detection and correction for matrix effects.

As discussed in the introduction, this advantage makes the technique rather unique, since it is hard to find other any other solid sampling techniques that can rely on a simple calibration scheme using aqueous standard solutions only. However, there is a price to pay for it. In order to obtain signals that are truly comparable (at least in terms of integrated peak area) regardless of the matrix, it is typically necessary to carry out some optimizations on the best temperature conditions and on the most suitable chemical modifiers. In other words, some method development is needed for every particular combination of analyte and matrix. This method development may be very straightforward and require only a couple of hours (e.g., determination of a non-volatile analyte -Fe, Ni, Co, Cu, Cr, etc.- in a volatile sample such a any polymer), but it may also be more complicated, requiring days to weeks (e.g., determination of a volatile element, such as Hg, in polymers).[30] In any case, this aspect leads to a simple conclusion. If a laboratory receives a sample that needs to be analyzed only once, it is probably not worthwhile to attempt the development of a SS HR CS GFAAS method; instead, only when analysis of such type of sample is expected to be demanded many times in the future it is advisable to invest the time needed to develop a robust SS HR GFAAS method in order to save a lot of time and effort in the long term, as practically no sample preparation/digestion will be required.

This advice was also valid for LS SS GFAAS. However, it has to be stressed that the use of SS HR CS GFAAS makes it easier and faster to develop a new method, and can provide satisfactory results in situations in which it was hardly possible for LS instruments to do so, as will be discussed in section 3.

Other traditional disadvantage associated with SS GFAAS is the (relatively) poor precision often found. No improvements have been reported in this regard, because this characteristic is inherent to the technique. Since the amount of sample introduced into the furnace is typically of a few milligrams or less, the precision obtained will simply reflect its homogeneity at this level.[31] This could be considered as a problem for bulk analysis, although it can also be considered as an advantage if the goal is to investigate the distribution of the analyte in the sample at the mg or sub-mg level. In fact SS GFAAS has been used for many years to study and characterize the degree of homogeneity of, for instance, certified reference materials.[32,33] In any case, it is important to highlight that, eventually, the precision finally obtained will depend on the number of replicates. Thus, the analyst will always have the choice to improve precision by increasing this number. The key issue is to obtain a sufficient precision with a number of replicates that is still low enough such that it is still faster to obtain the results in comparison with any alternative approach (e.g., sample digestion). In general, carrying out 5 replicates per sample, and using the median to minimize the influence of outliers,[34] permits obtaining RSD% values in the 5-10% range in most situations. Another conclusion can be derived from this point. If extreme precision is required (2% or better), then SS HR GFAAS is probably not the technique of choice, although it might not be easy to find a technique that can deliver such overall precision at trace levels.

Another disadvantage to discuss is the limited multi-element potential that HR CS GFAAS currently shows. The crucial aspect is that the instrumentation commercially available provides a continuous and high intensity emission over a large spectral interval (from 190 to 900 nm), allowing for the monitoring of atomic absorption signals with high spectral resolution (a few picometers). However, only a narrow spectral region (from 0.2 to 1.0 nm, depending on the wavelength) can be simultaneously monitored with the instrumentation currently available. Thus, truly simultaneous multi-elemental analysis is usually only possible for a few elements, which must show closely adjacent lines.[24] This is a clear drawback when compared with other analytical techniques, but it is in fact an advantage in comparison with LS GFAAS devices, which typically exhibit no multi-element potential at all (except for some particular instruments that are no longer commercially available[12]). Thus, SS HR CS GFAAS is particularly useful in cases where the number of target analytes is small.

Finally, an important advantage is that the characteristics of the HR CS instrument enable the quantitative monitoring of the molecular absorption (MAS) of diatomic molecules as well, which can be used to determine some non-metals (e.g., Br, Cl, I, F or S) that were not directly accessible before using LS GFAAS.

Having all these aspects in mind, different situations in which application of a direct method with HR CS GFAAS is useful can be identified: i) trace and ultratrace determinations, taking advantage of the high sensitivity of the technique, the absence of sample dilution and the reduced contamination/loss risk. SS HR GF AAS can be particularly helpful when a few analytes have to be monitored only and sample throughput is more important than obtaining a very

high precision. Alternatively, for samples very difficult to digest (e.g., graphite, ceramics or carbon nanotubes), then SS HR GFAAS may not be only a faster alternative to a conventional digestion approach, but one of the few ways in which it may be possible to achieve accurate values, especially if no matrix-matched standards are available for calibration, as required for most of the other solid sampling techniques. Finally, determination of non-metals at low levels is always complicated, and SS HR GFMAS offers new possibilities in this field, which is still developing.[21,25,26] ii) studies concerning the spatial distribution of the analyte within the sample. As discussed before, the method has been used for the study of the homogeneity of certified reference materials (CRMs).[35] iii) different situations in which only a small sample amount is available. In this field, for instance, some examples of analysis of individual specimens of small invertebrates have been presented.[36,37]

3. Strategy to develop a method for direct analysis with HR CS GFAAS

There are some obvious differences when developing a method aiming at the direct analysis of solids or complex samples in comparison with the analysis of digested/diluted samples, and this section will try to give a summary of those, while also highlighting the benefits of HR CS instrumentation in comparison with traditional LS devices.

3.1. Sample pretreatment

Obviously, the philosophy of direct analysis dictates that pretreatment of the sample should be avoided whenever possible, in order to retain most of the advantages presented in **Figure 3**. As discussed before, the characteristics of the technique favor this approach, as it can deal with very different types of samples (powders, chips, discrete pieces of all types of materials).[38] The most

usual pretreatment step that might be necessary to consider is drying, particularly for analysis of biological materials, since it is typically required to refer the final result to the dry mass (although sometimes for screening purposes that is not even necessary[39]). Other samples only require cutting into pieces of suitable size for the graphite furnace (e.g., polymers). As a general rule, sample grinding (which is almost compulsory when opting for slurries) should only be undertaken when it is really necessary (e.g., when justified by a significant improvement in precision, which sometimes is not as high as anticipated[31,40]). Again, if a sample requires extensive sample pretreatment it has to be reconsidered if SS HR CS GFAAS is the right technique for its analysis.

3.2. Selection of sample mass

In theory, this appears to be a key issue. Of course, a higher sample mass means a higher signal for the analyte, but also a higher amount of matrix present in the furnace, which increases the risk of interferences. On the other hand, if the sample is too small, heterogeneity may have an impact on the results.

In practice, however, the choice is restricted by the dimensions of the platform. The current ones are approx. 1 cm long and less than 2 mm deep only. Thus, typically a few milligrams is the maximum amount that can be loaded onto them, depending on the sample density. The limit for lower masses is set by the balance (precision 1 µg), but it has to be stated that it is not vey comfortable to manipulate samples that are smaller than 0.05-0.10 mg. Some examples of work with microsamples are discussed elsewhere.[36,37] Therefore, those are the parameters more often used in the literature (between 0.1 and 5 mg). Within

this range, the analyst can choose the optimal value in order to adapt the sensitivity. However, other practical considerations have to be taken into account. For instance, analysis of an organic sample is typically simple, as most of the matrix can be eliminated during the pyrolysis step (just by using a sufficiently high temperature or even by adding O_2, if necessary). Thus it is not problematic to deposit a relatively large amount. However, there are other matrices that will strongly interact with graphite (e.g., AlO_2 or SiO_2[41,42]) and, as a consequence, the platform and the tube will rapidly deteriorate, which translates into a higher economic cost per analysis. While this issue can be somewhat balanced by using some modifiers to enhance the lifetime of the graphite parts (e.g., addition of graphite powder), it may be recommended to use smaller sample masses for such type of samples.

Moreover, in some cases it has been reported that using very high masses can lead to inaccurate results when calibrating *vs*. aqueous standard solutions, possibly owing to incomplete atomization.[43,44] Also some inaccuracies for very low masses have been reported, although most information on this subject was obtained with older (line source) instrumentation, using much larger graphite platforms or boats.[45]

Overall, this is a parameter that needs some optimization within the values presented above to achieve sufficient (but not excessive) sensitivity, minimal matrix effects, sufficient precision and a reasonable tube lifetime.[46,47]

3.3. Selection of instrumental parameters

This part refers to the instrumental parameters, except for the temperature program, which will be discussed specifically in the next section. The criteria for selecting some of these parameters (e.g., wavelength, Ar flow) is clearly

different for direct analysis or for analysis of samples digested and/or diluted. While for diluted samples the most sensitive conditions are always selected, since in the case of obtaining a signal outside of the linear range it is simple to further dilute the sample (and some instruments can even do so automatically), that is not the case when truly direct analysis is attempted (in contrast with slurry sampling, which also enables diluting the sample as required). Therefore, and taking into account the narrow linear range that characterizes atomic absorption, with LS instruments it was very often necessary to look for alternative less sensitive lines of the analyte when it was not present at very low levels in the target sample. The maintenance of the Ar flow during the atomization step was another solution frequently used to decrease the sensitivity (although it could also help in minimizing some gas-phase interferences[48,49]), and other approaches (e.g., using the 3-field mode Zeeman-effect background correction[50]) were also explored. This is one of the aspects where the introduction of HR CS AAS instrumentation has improved the situation more significantly and in various ways.

First of all, HR CS AAS makes the use of alternative, less sensitive lines more suitable. This is simply because this instrument provides a continuous and high emission intensity in all the range 190-900 nm, as indicated before (the spectral radiance of the Xe lamp decreases below 230 nm,[8] but even in this region the remaining radiance is always 2 orders of magnitude higher than that of hollow cathode lamps). Therefore, as a consequence, all lines, resonant or not, will show a high and similar lamp energy, as opposed to hollow cathode lamps, where weaker lines where more noisy.[22] A clear example of this beneficial issue applied to solid sampling was presented by Araujo *et al*.[51] The authors

attempted the direct determination of Sb in airborne particulate matter collected on glass fiber filters and succeeded using a Sb secondary line (212.739 nm). However, attempts to translate the method to a LS device failed, because this line is very weak (20 times less sensitive than the main line) and the spectrum obtained was too noisy.

Another novelty introduced with the HR CS AAS is the increased potential to monitor multiplets. Traditionally, with LS instruments, appearance of multiplets was problematic because the combined absorption of all the multiplet lines was actually measured (unless the difference between the lines was high enough such that the resolution of the monochromator allowed for the selection of only one of them). As a consequence, the resulting linear range was usually even narrower. However, the resolution provided by the HR CS AAS instrument permits to measure every line of the multiplet separately. In this way, if the different lines of the multiplet show very different sensitivities, it is possible to expand the linear range very easily. In fact, the analyst can select the line most suitable for every particular sample, and this can be done when processing the data, without any need to perform additional measurements. **Figure 5** shows how this feature can be use to extend the linear range for the determination of Ni.[52] An example of this possibility applied to solid sampling was published by Lepri *et al*., who reported on the simultaneous monitoring of the 344.099 nm and 344.388 nm lines for Fe, and the 232.003 nm and 232.138 nm lines for Ni, in order to expand the working linear range for the analysis of charcoal and carbon black.[53]

Appearance of these multiplets cannot be considered as very infrequent when monitoring atomic lines (particularly for those elements that show more lines

such as Co, Cr, Fe, Mn, Ni, and Ti), but it is certainly not the rule. However, this is in fact the most common scenario when using a graphite furnace for determining non-metals (e.g., halogens, P, S). In that case, the rotational hyperfine structure of molecular electronic transitions is typically monitored, such that several spectral "lines" are often available, as shown in **Figure 6** for the CaBr molecule. This aspect can be used to increase the linear range in the same way as described for atomic multiplets.[54] Application of this aspect to direct solid sampling was recently described by Flórez and Resano[55] for Br determination in polymers.

In any case, while this solution is not really universal, it is actually quite relevant to be able to access to all the information and make the final calculations *a posteriori*, without the need for further measurements. This aspect is particularly important when aiming at the analysis of microsamples that can only be analyzed once.[36] However, even when that is not the case, it is a significant feature, because the traditional situation was that, whenever any sample fell outside the linear range, the analyst had to look for alternative conditions, and, if available, repeat the measurements, including a new calibration curve in those new conditions, all of which was against the basic principle of obtaining results faster.

A more universal approach that can also be used with HR CS AAS is the selection of the suitable number of detector pixels to quantify the signal. The CCD detector used in this instrument possesses 588 pixels, but only 200 of them are used to monitor the spectral area of interest (the rest are used for internal corrections). Usually, an atomic line is completely covered by 7-9 of these pixels (approx. 10 pm, depending on the wavelength and conditions), but

the analyst has all the freedom to select which ones are used for quantification. Normally, for best limits of detection (LOD), only the most sensitive central pixels should be used (typically 3 pixels, the central plus the two adjacent ones), as discussed by Heitmann *et al*.[56] and confirmed in other works aiming at direct solid sampling.[30,57] However, side pixels can be used to expand the linearity.[56,58] The trend observed is that, when introducing very high amounts of an analyte, the atomic signal broadens very significantly, such that even when the signal becomes saturated for the central pixels, it is still feasible to obtain well-defined temporal signal profiles using side pixels. Some examples of this feature applied to solid sampling have been published in the literature.[36,37,55,59,60] **Figure 7** illustrates this issue for a situation in which very small invertebrates (*Daphnia magna*) exposed to Ag nanoparticles were analyzed. Each of these specimens could be monitored only once owing to the destructive nature of the method, so there was no possibility to repeat any measurement under alternative conditions. Still, use of side pixels permitted to cover a vast linear range (from 3 up to 100 000 pg, as shown in **Figure 7c**), which could even be further expanded by using other pixels that were further away from the center.

In principle, this solution can always be used (alone or in addition to the other ones discussed before), which represents a significant step forward for direct solid sampling analysis.

Finally, another important issue to consider regarding wavelength selection is the possibility to perform simultaneous multi-element analysis. This is again a novel feature of HR CS AAS. Even though, as discussed in section 2, the capabilities of the currently available instrumentation are limited in this regard

because the spectral range that is simultaneously monitored is very narrow, there are still some circumstances in which it is possible to develop these multi-element methods. For that, it is necessary to find atomic lines of the target elements that are sufficiently close (within 0.2–1.0 nm, depending on the wavelength). The difficulty in finding these lines depends on the target elements, because there are some elements with hundreds of usable lines available in the UV–vis area, such as Co, Cr, Fe, Ni or Ti,[22] while other show only a few lines (for instance, most metalloids).

In addition to finding lines that are close enough, the lines finally selected must be suitable in terms of sensitivity for the contents of all the target analytes. This is a serious limitation when direct analysis is aimed at, because some of the solutions discussed before to adapt the sensitivity when performing mono-element determinations (e.g., keeping the Ar flow during the atomization step) may not be appropriate for a simultaneous multi-element approach, as they will have an effect on all the analytes. Again, in this case, use of the side pixels appears to be a better solution, because it enables adjusting the sensitivity selectively for every line monitored.

An example of this situation was a method for the simultaneous and direct determination of Co, Fe, Ni and Pb in carbon nanotubes. In this case, it was possible to find suitable lines that were close enough for the 4 analytes and, by selecting the right pixels, samples showing different contents could be analyzed.[35] Moreover, for Co not only one but two lines (see **Figure 8**) were measured, thus also permitting to adapt the sensitivity, if required, by choosing the line more suitable for every particular sample.

Other works in which the use of side pixels for simultaneous and direct multi-element analysis was demonstrated include the article by Dittert *et al*.,[59] aiming at the determination of Co and V in undiluted crude oil, and the article by dos Santos *et al*.,[60] in which the simultaneous determination of Cd and Fe in soil samples was carried out using this strategy.

Summing up, the monitoring of multiplets and the more universal approach of choosing side pixels are valid strategies to adapt the sensitivity of the method developed to the actual analyte content in every sample, thus helping in solving one of the traditional problems of LS SS GFAAS, and doing so when processing the data, without the need to repeat any measurement.

3.4. Selection of atomization/vaporization conditions

This was typically the most relevant issue for developing a SS GFAAS method with LS devices, and still is a critical aspect, but again HR CS GFAAS offers very significant advantages in this regard.

Essentially, three different situations can be encountered when developing a SS GFAAS method: a) The analyte is less volatile than most of the main matrix components; b) The analyte is more volatile than most of the main matrix components. c) The analyte shows a volatility that is similar to that of the main matrix components.[29]

The ultimate goal when developing a solid sampling method using GFAAS is always to try to achieve the selective atomization of the analyte, because, if the atomization of the target element is separated in time from the atomization/vaporization of most matrix components, matrix effects can be greatly minimized to a point that it may be possible to obtain a signal

comparable with that of an aqueous standard solution, thus greatly simplifying calibration.

In this aspect, situation a) can be regarded as relatively simple. In fact, it may be the situation most often investigated in the literature. Usually, optimizing the pyrolysis step properly, it is possible to remove most of the matrix leaving the analyte ready for atomization. This is the case when determination of many transition metals in biological samples or polymers is intended. Many examples of this case (using LS) can be found in this review.[38] Some examples using HR CS GFAAS have also been published.[36,61,62]

Situation b) is also not so complicated. In this case, the pyrolysis step is not so critical (it might even be omitted or, at least, shortened), because removal of matrix components will not be easily achieved. Instead, the key issue in this case is to optimize the atomization temperature such that it is possible to atomize the analyte before most of the matrix components are vaporized, thus avoiding matrix effects. This case is found when the determination of a volatile analyte, such as Hg, is attempted in, for instance, geological samples. Or when analysis of very refractory samples (e.g., ceramics or some metals) is intended. Again, there are several examples of this situation explored in the past,[42,63-65] and also more recent cases using HR CS GFAAS.[47,66-68]

However, it is when confronted with situation c) that the use of HR CS GFAAS really helps. Obviously, this is the most complicated situation, as interferences are expected to occur. The solution, in this case, often requires the use of a suitable chemical modifier. By using such modifier, either to selectively alter the volatility of the analyte species (e.g., addition of Pd to stabilize a volatile element during the pyrolysis) or of the major matrix component (e.g., addition of

an acid, or of O_2, to help in decomposing the matrix), and after optimization of the temperature program, it could be possible to achieve either situation a) or b).[35,46,69]

Use of HR CS GFAAS brings some advantages in this latter case. First of all, with this technique, a three-dimensional, time- and wavelength-resolved absorbance signal is recorded (e.g., see **Figure 6a** or **8a**). All the events occurring in the vicinity of the target line are directly observed. Thus, spectral overlaps are directly detected (it is extremely unlikely that they match completely the signal of the analyte both spectrally and temporally), and it becomes very simple to track the interferences during the optimization of the temperature program to find the optimum condition, in which they may be avoided or resolved in time.[47,68,70]

In addition to this remarkable feature, it may be possible to correct for overlaps even when it is not feasible to resolve them temporally or spectrally. The HR CS AAS instrument operates like a double-beam device, such that all the events that affect the flux of radiation of all the pixels simultaneously and to the same extent are automatically compensated. That means that all those events that can be considered as continuous in the short wavelength interval that is measured, such as radiation scattering, lamp flickering or temporal changes in the transmittance of the gas phase, can be effectively corrected for, leading to a much more stable baseline (and ultimately to a better LOD). Several examples of these benefits applied to direct solid sampling have been reported.[30,47,66,68,70,71]

This correction for continuous events is carried out automatically by the instrument software. However, there is still the remaining issue of spectral

overlaps produced by absorption of radiation from other species. Frequently this problem is caused by the formation of the diatomic molecule of an ubiquitous element, such as CS, NO, PO or SiO. For these cases, it is still possible to identify the interfering compound, obtain a reference spectrum, and accurately subtract it from the sample spectrum by means of a least-squares background correction algorithm (LSBC), such that a reliable value can be obtained.

An example of this strategy is shown in **Figure 9**. In that work, determination of Au in mice brain (after exposition of the animals to Au nanoparticles) was intended.[72] The signal for Au seemed to be affected by some spectral interference (see **Figure 9a**). In the spectral region surrounding the main Au line, it is well-known that PO may absorb, so a reference spectrum was obtained with a phosphate solution. Such a spectrum is shown in **Figure 9b**. A good correspondence between the peaks of the interference present in the sample (see **Figure 9a**) and those of the reference spectrum can be appreciated, thus further confirming the identity of the interfering molecule. Because the relation between the intensities of all the PO transitions should always be constant (only subject to small experimental errors), based on the signals obtained for PO transitions that do not overlap with the Au atomic line, it is possible to proportionally subtract the portion of the PO signal that overlaps with the Au signal in every sample replicate using this least squares algorithm. In this way, the corrected spectrum should show only the net atomic absorption of the target analyte, with a stable baseline, as shown in **Figure 9c**.

LSBC has demonstrated to work very efficiently, even in situations in which the interfering signal is significantly higher than that of the analyte. As it occurs with any mathematical approach, the key is that all the transitions are truly

simultaneously monitored, because if a sequential method would be used any variations occurring during the alternate measurements might significantly affect the final results.

Several applications reporting on the use of LSBC have been described in the literature since the first article published by Becker-Ross *et al*. dealing with the determination of As and Se in urine,[17] and many of these articles were devoted to the development of methods for direct analysis.[18,40,53,71-74] In this regard, the article published by Araujo *et al*. is noteworthy, further confirming that this approach could be used even in cases in which more that one interfering species is found.[40] In such case, the sequential correction using the reference spectra of both interfering molecules (SiO and PO) permitted to directly determine the analyte (Sb) in sediments.

In addition to this significant improvement, there are two new aspects to consider when developing a method using SS HR CS GFAAS when compared to LS instrumentation. One is the possibility to determine several elements simultaneously. This requires that the lines selected are very close, which represents a serious limitation, as already discussed in detail in section 3.3. But moreover, it requires the development of a temperature program and the addition of a chemical modifier that is suitable for the simultaneous monitoring of all of the target analytes. This may be easy to do if these elements show similar thermochemical characteristics, but may require the use of compromise conditions if their characteristics differ significantly.

For the latter situation, an alternative possibility is to attempt the sequential monitoring of the analytes, in a way that still enables achieving all the information from every individual replicate. That is, atomizing and monitoring

the elements sequentially after a single sample deposition. One relevant advantage of this strategy is that different parameters (e.g., temperature, wavelength or even the chemical modifier) can be selected for every atomization step, being thus possible to use optimal conditions for each particular analyte. This approach was demonstrated for the direct determination of Cd and Ni in biological samples in ref. 52, and was later implemented also for the direct determination of Cd and Cr in biomass.[75]

Finally, there is a novel possibility to quantify non-metals based on the monitoring of their molecular spectra. Again, this feature was discussed in section 3.3. However, it is important to stress that the method development is a bit different when vaporization and not atomization is intended. Generally, speaking, it is necessary to find molecules that are stable enough at the temperatures typically used in a graphite furnace and that absorb radiation in the 190-900 nm range with sufficient sensitivity. These target molecules may be spontaneously formed in a graphite furnace (e.g., CS, used for S determination, or PO, used for P determination,[76] since C and O are always available in high amounts in a graphite furnace). However, that is not always the case, as it typically occurs when aiming at the monitoring of halogens as AlCl, CaBr, GaF or BaI, to name a few of the more popular species used so far. Then, addition of a reagent (e.g., containing Al, Ca, Ga or Ba for the examples listed before) may be necessary, besides the addition of any chemical modifier needed to stabilize the original analyte species. Moreover, in this case, competition with other species present in the samples must be considered. For instance, it is possible to determine Br as CaBr in different polymers,[55] but if the polymer contains a large amount of Cl, then the situation becomes more difficult, because

formation of CaCl (bond dissociation energy 409 KJ mol^{-1}) and not of CaBr (bond dissociation energy 339 KJ mol^{-1}) will be favored, as it is a more stable molecule. Thus, the chemical composition of the sample needs to be taken into account when selecting the target molecule to minimize the risk of interferences; and the less stable the target molecule, the more prone it will be to suffer from these interferences. Still, different works have demonstrated that it is feasible to directly determine non-metals in solid samples using HR CS GF MAS and calibrate with aqueous standard solutions.[55,57,77-81]

There are different reviews available in the literature on the monitoring of non metals using HR CS GFMAS where more information can be found,[21,25,26] the last one being also quite tutorial in nature. However, it can also be mentioned that one of the advantages of using MAS is that the use of milder temperature programs is feasible, since only vaporization is required, which represents a gain in terms of the lifetime of graphite pieces.

In conclusion, the use of HR CS CFAAS makes it simpler and faster to develop the appropriate temperature program for direct analysis, as everything that occurs in the spectral region surrounding the analyte signal can be directly seen. Moreover, the superior background correction capabilities of HR CS CFAAS enable the development of methods in situations in which obtaining accurate results with conventional LS instrumentation would hardly be feasible.[30] Finally, the technique offers some more advanced features (multi-line monitoring, monitoring of the molecular spectra) for which method development may be a bit more complex, but that offer unique possibilities (multi-element determinations, direct quantification of non-metals) beyond the capabilities of traditional LS devices.

3.5. Calibration

It has already been discussed in section 2 that the vast majority of articles devoted to direct analysis of solid samples and complex matrices have opted for using the most straightforward calibration approach, just constructing the calibration curve with aqueous standard solutions.

Obviously, even if a quite selective vaporization/atomization process is achieved, it is hard to expect exactly the same mechanism to take place for a solid sample and for an aqueous standard solution, which often results in differences in the signal profiles obtained for them. However, if complete vaporization/atomization is attained and the temperature of the furnace does not change significantly during the duration of the signals, the integrated peak areas may still be comparable. **Figure 10** shows a typical example of this situation, found during determination of S in various solid CRMs. The profile obtained for the solid samples is a bit delayed and often broadened, as it is more difficult to liberate the analyte from the remaining of the matrix, but still the peak areas finally computed are very similar.

The use of HR CS GFAAS instrumentation also brings a new possibility to further minimize matrix effects and improve the precision, and that is the use of an internal standard. This strategy has not yet been used in any determination in which direct analysis was attempted, but can be considered if unsatisfactory results are obtained when using aqueous standard solutions for calibration. The requisites for finding a suitable internal standard are discussed in detail elsewhere.[52]

3.6. Data treatment

This step has also changed significantly with the use of HR CS GFAAS. The traditional issues still need to be considered. Establishing the optimum number of replicates to achieve sufficient precision while keeping a reasonably high sample throughput is important, as discussed in section 2. If the number of replicates is low (e.g., 3 or 5), as it is most often the case, then attention has to be paid to the possible appearance of outliers and their impact on the final value. For this situation, use of the median instead of the mean as representative value has been recommended.[34]

However, there are new operations that are performed during this step. Most of them have already been commented throughout section 3: i) the selection of the number and position of the detector pixels used for quantification conditions the sensitivity, LOD and also the linear range (see section 3.3. and **Figure 7**),[56] and thus this is very important for direct analysis since samples cannot be diluted; ii) the use of LSBC can serve to correct for spectral overlaps, leading to improved accuracy for complex samples (see section 3.4. and **Figure 9**); iii) the simultaneously monitoring of various lines is possible, opening possibilities for multi-element determinations, or, if the different lines belong to the same species, to expand the linear range easily (see section 3.3. and **Figure 5**).

It is interesting to stress that, in the latter case, expanding the linear range is feasible only when the lines monitored show very different sensitivities. There are other cases when various transitions of relatively similar sensitivity are available, which occurs when monitoring some diatomic molecules (e.g., CS or PO). **Figure 11** shows an example of the CS spectrum. Obviously no significant gain regarding the working range can be obtained then. However, this situation may also be beneficial. Instead of using one line for the determination,

combining the signal of several of these lines may serve to improve the LOD to some extent (up to a factor of 3, depending on the number of lines summed has been reported[55-57,76,78]) and also to decrease the imprecision,[76] which has also been demonstrated for direct analysis of solid samples.[55,78]

The difficulty in monitoring this dense spectrum is that there are so many transitions and they are so close that the software of the instrument may have difficulties in properly setting the baseline if the automatic (named dynamic) mode is chosen (see **Figure 11b**).[82] Thus the manual (or static) mode, where the analyst defines the valleys of the peaks, is often preferred (see **Figure 11a**). In this regard, it can also be mentioned that a recent software update provides a new baseline correction algorithm call IBC (iterative baseline correction). While the exact details of this algorithm are not available yet, its application helps in reducing the width of the lines at the cost of also lowering their maximum value, as shown in **Figure 11c**. Thus, it becomes simpler to set the baseline for the software. Moreover, this approach may be recommended to avoid some spectral overlaps, even though no article has yet reported on its use, but this may simply reflect the fact that it is a very novel feature.

Overall, it can be stated that, with HR CS GFAAS instrumentation, the quality of the results finally achieved depends significantly on data treatment. The technique provides much more information that traditional LS devices and off-line data treatment is key. This may be seen as an advantage, because the potential of today's hardware and software packages permits to extract and deal with all this information in a fast way.

4. Direct analysis by means of HR CS GFAAS: applications

Tables 1 to **3** collect all the information relative to the articles published to date devoted to direct sample analysis (including slurries) by means of HR CS GFAAS. The tables have been categorized into the same groups as is customary for JAAS Atomic Spectroscopy Updates (ASU): Metals, chemicals and materials (**Table 1**); Clinical and biological materials, foods and beverages (**Table 2**); and Environmental (**Table 3**).

When examining all the applications, some trends can be observed. Indeed, several of the articles published earlier were focused on comparing the possibilities of HR CS GFAAS with those of LS GFAAS devices.[18,30,83,84] On the other hand, more recent articles have attempted to develop more complex applications, even taking advantage of the potential of the technique to determine non-metals by monitoring molecular spectra. Several articles have demonstrated that it is feasible to determine these non-metals directly using this approach, after the first article published in 2009,[57] which compared the use of atomic or molecular spectra to determine P. Most of these works have studied S determination,[77-80,85] but, recently, also satisfactory results for Br[55,81] and F[86] have been reported. This area is expected to continue growing, because there is still fundamental research to be carried out on this topic, as the mechanisms of formation of molecules are not clear yet (e.g. are they formed in gas phase or in condensed phase?).[81] Besides, as discussed in section 3.4., the development of these methods requires the use of several modifiers and reagents, as it is both necessary to stabilize the primary compounds during pyrolysis (which is not always easy as many of these compounds are very volatile) and to make sure that formation of the target molecule is promoted. Sometimes, even the order of addition of the modifiers/reagents is important to

guarantee an efficient interaction.[86] Thus, overall, method development in these cases entails more effort, sometimes requiring the use of new strategies (e.g., use of nanoparticles as modifier,[78] or evaluation of the chemical form of the target element that is more suitable to prepare the aqueous standard solutions for calibration[77,79]). Nevertheless, the determination of these analytes is very challenging for most techniques, such that the development of fast, straightforward and sensitive methods is very relevant.

Another topic that has been investigated only in recent years is the development of methods for direct analysis of nanomaterials[35] or for the monitoring of nanoparticles in biological or vegetal tissues.[37,72] HR CS GFAAS shows potential to provide significant information in this field, permitting analysis of individual micro-specimens or investigating the distribution in different areas of a tissue, as well as great sensitivity to detect the nanoparticles most commonly investigated (e.g., Ag and Au). Moreover, the first results indicating that it may be possible to differentiate between nanoparticles and ionic species by extracting information from their temporal signal profiles have been recently published.[87] There are other techniques that can provide this type of information, but most of them require performing some sample treatment (e.g., dissolution), which always represents a serious risk, as it is hard to preserve the exact way in which the analyte is present throughout this process. However, with HR CS GFAAS, this study can be applied directly to solid samples.

A pioneering work on this topic evaluating the direct detection of Ag nanoparticles in parsley has been published very recently by Feichtmeier and Leopold.[88] It has been reported that it may be possible to establish if Ag nanoparticles or Ag ions are present in parsley (calculating the atomization

delay, normalized to the sample mass) and even the size of the nanoparticles (evaluating the atomization rate). This is all based on the fact that nanoparticles and ionic species do not atomize exactly at the same time (they may interact with the matrix in a different way) and that, for nanoparticles, the heat transfer is slower as their size increases, thus affecting their atomization rate.

A significant number of applications have targeted the determination of several analytes. For such case, a variety of options have been explored. In some cases, the determinations have been conducted separately, one element at the time, as it would be typically done with LS GFAAS.[53,89-92] In other cases, a sequential approach has been used, but in such a way that all the analytes were measured in every single replicate, so it can be considered as a *quasi* simultaneous approach, as it does not require any additional sample measurements. This strategy typically involves using two different atomization steps, the first one for the most volatile element and the second one for the most refractory one. Examples of this strategy include the measurement of Cd and Fe in different samples (grain, bean, soil and sludge).[60,67,93] In these cases, the same spectral area that included the two target lines (one for Cd and one for Fe) was monitored during both atomizations steps. However, as discussed in section 3.4., if such sequential approach is intended, it is possible to monitor different spectral regions in every atomization step, such that there is no limitation for selecting atomic lines (they do not need to be very closely located). This approach was demonstrated for the determination of Cd and Ni in white cabbage,[52] and was further used for the determination of Cd and Cr in biomass.[75] Finally, some articles have reported true simultaneous determinations (all the analytes are measured during the same atomization

step), such as Cr and Fe in crude oil,[94] Co an V in crude oil as well,[59] Co, Fe and Ni in Oyster tissue,[52] Cd and Ni in cabbage (comparing the results with the sequential approach mentioned above),[52] Mo and Ti in urine deposited onto clinical filter papers,[95] Co, Fe, Ni and Pb in carbon nanotubes[35] and Fe and Ni in pine needles and lichen.[74]

Many examples have demonstrated how the possibilities discussed in detail throughout section 3 are critical for direct sample analysis. In this regard, a few aspects can be stressed such as: i) monitoring the spectra surrounding the analytical signal as a function of time in order to develop a method that is interference-free;[47,68,70] ii) use of LSBC to correct for spectral overlaps;[18,40,53,71-74,96,97] iii) use of side pixels[35-37,59,60] and/or simultaneous monitoring of two lines of the same analyte[35,52,53] to adjust the sensitivity. Thanks to these possibilities, it can be seen that the vast majority of applications developed reported accurate results simply constructing the calibration curve with aqueous standard solutions, for a large variety of analytes (metals, metalloids and non-metals) and samples (blood, carbon nanotubes, coal, crude oils, dust, glass filters, sediments, soils, polymers, vegetal and biological tissues, etc.).

5. Conclusions

The development of methods for direct sample analysis using GFAAS still requires some expertise to carry out all the required optimizations. However, the arrival of HR CS GFAAS not only has made it possible to develop applications that were not feasible before (e.g., direct determination of non-metals or simultaneous multi-element analysis, in some cases), but it permits to reach the optimum conditions in a simpler and faster way, because all spectral events taking place in the region surrounding the analyte signal are directly observed.

Moreover, many traditional problems related with direct sample analysis (absorption of concomitants, sensitivity adjustment) can now be solved off-line by treating the data properly, thus further limiting the number of measurements needed to develop a new method.

Concerning future research, the development of HR CS GFAAS instrumentation enabling the monitoring of a much wider spectral region simultaneously would obviously enhance the potential of the technique for multi-element applications. Until such instrumentation is available, more developments related with the determination of non-metals are expected,[25,26] perhaps together with more works exploring the intriguing possibility to differentiate between nanoparticles and ionic species.[88]

Acknowledgements

This work has been funded by the Spanish Ministry of Economy and Competitiveness (project CTQ2012-33494) and the Aragón Government (Fondo Social Europeo).

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Figure captions

Figure 1. Setup of a high-resolution continuum source atomic absorption spectrometer. Reproduced with permission of Elsevier (http://www.sciencedirect.com/science/article/pii/S0584854713001596).[24]

Figure 2. a) Number of publications that have reported the use of high-resolution continuum source graphite furnace atomic (or molecular) absorption spectrometry either for direct analysis or after sample treatment. **b)** Comparison of the number of publications that have reported on direct sample analysis in a graphite furnace, either using a continuum (Xe) lamp or a hollow cathode line as radiation source. Source: ISI Web of Science. Papers that appeared in proceedings, book chapters and reviews are not included. Review articles are also not included.

Figure 3. Main advantages and disadvantages of solid sampling high-resolution continuum source graphite furnace atomic (or molecular) absorption spectrometry.

Figure 4. Graphite platform containing a solid sample that is transported to the graphite furnace for subsequent GFAAS analysis by means of a fully automated device (Analytik Jena SSA 600).

Figure 5. Wavelength-resolved time-integrated absorbance spectrum showing the Ni triplet located in the vicinity of 234.6 nm obtained for an aqueous solution containing 10 ng of Ni *via* HR CS GFAAS. The linear range of every line of the triplet is also shown. Reproduced with permission of Elsevier (http://www.sciencedirect.com/science/article/pii/S0584854711000590).[52]

Figure 6. A) Time and wavelength resolved molecular absorbance spectrum of CaBr obtained for the vaporization of 100 ng of Br by means of HR CS GFMAS

with the spectral window centered in 624.982 nm. B) Same signal as in A) but time-integrated. Reproduced with permission of Elsevier (http://www.sciencedirect.com/science/article/pii/S058485471300222X).[55]

Figure 7. A) Absorption line profiles obtained for 250 pg of Ag at 328.068 nm. The profile has been segmented such that the exact portion of the signal monitored by every detector pixel can be appreciated. B) Absorption line profiles obtained for 100 000 pg of Ag at 328.068 nm. C) Linearity observed when monitoring the Ag 328.068 nm atomic line as a function of the detector pixels selected. The points highlighted in grey fall outside the linear range. D) Time-resolved absorbance signal measured at 328.068 nm obtained upon the atomization of 100 000 pg of Ag as a function of the detector pixel selected. Reproduced with permission of the RSC (http://pubs.rsc.org/EN/content/articlehtml/2013/ay/c2ay26456k).[37]

Figure 8. A) Time- and wavelength-resolved absorbance profiles in the vicinity of the 283.306 nm line obtained by direct atomization of a solid sample (0.151 mg of a carbon nanotube, which contains approx. 1 ng of Pb, 0.4 µg of Fe, 2.7 µg of Ni and 2.7 of µg Co). B) Same signal as in A) but time-integrated. Reproduced with permission of the RSC (http://pubs.rsc.org/EN/content/articlehtml/2013/ja/c3ja30377b).[35]

Figure 9. Wavelength-resolved time-integrated absorbance spectra obtained after HR CS GFAAS measurement of A) 2.558 mg of sample, brain tissue of a mouse exposed to Au nanoparticles; B) a 1% (m/v) $NH_4H_2PO_4$ solution; C) same signal as in A), after subtraction of the reference spectrum (shown in B) using least-squares background correction. Reproduced with permission of the RSC (http://pubs.rsc.org/en/content/articlehtml/2010/ja/c0ja00086h).[72]

Figure 10. Comparison of the time resolved absorbance measured at 257.958 nm obtained after the vaporization of a similar amount of sulfur from an aqueous solution or directly from various solid samples. Reproduced with permission of the RSC (http://pubs.rsc.org/EN/content/articlehtml/2012/ja/c2ja10322b).[78]

Figure 11. Time-integrated absorbance spectra obtained when monitoring CS transitions by HR CS GFMAS using different approaches to set the baseline for 50 ng of S. The zero level and the area below are highlighted in grey. The pixels that the analyst (static mode) or the software (dynamic mode) select to define the baseline are indicated by vertical lines. Reproduced with permission of Springer (http://link.springer.com/article/10.1007/s00216-013-7522-9).[26]

Figure 1

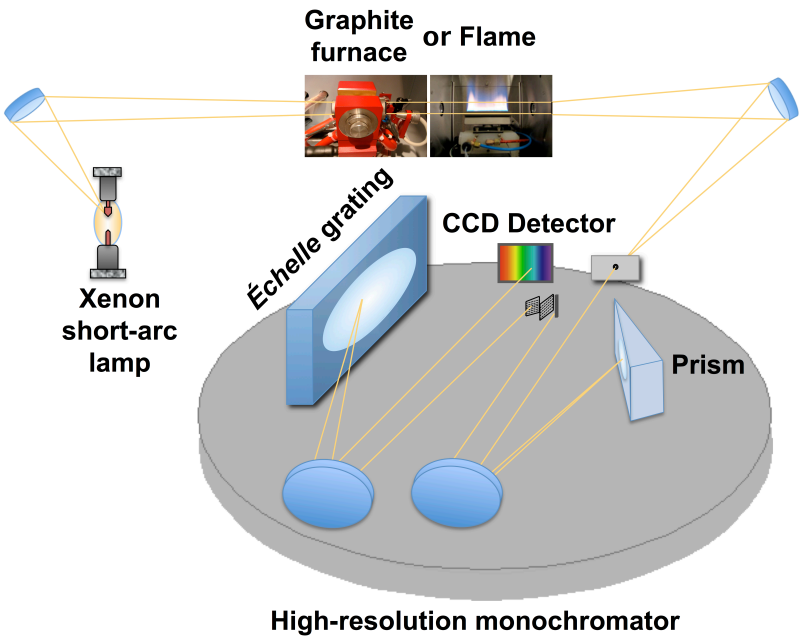

Figure 2

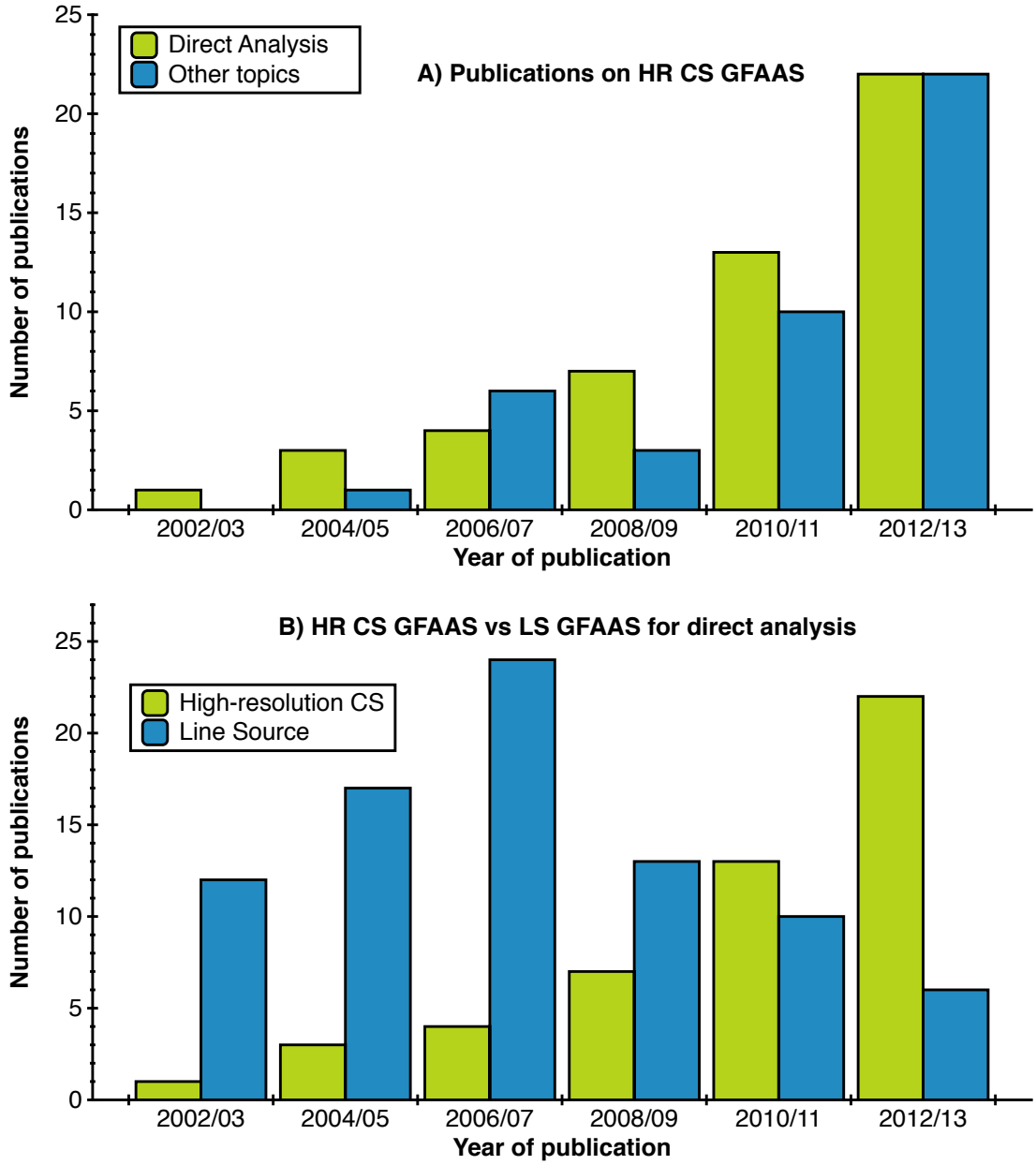

Figure 3

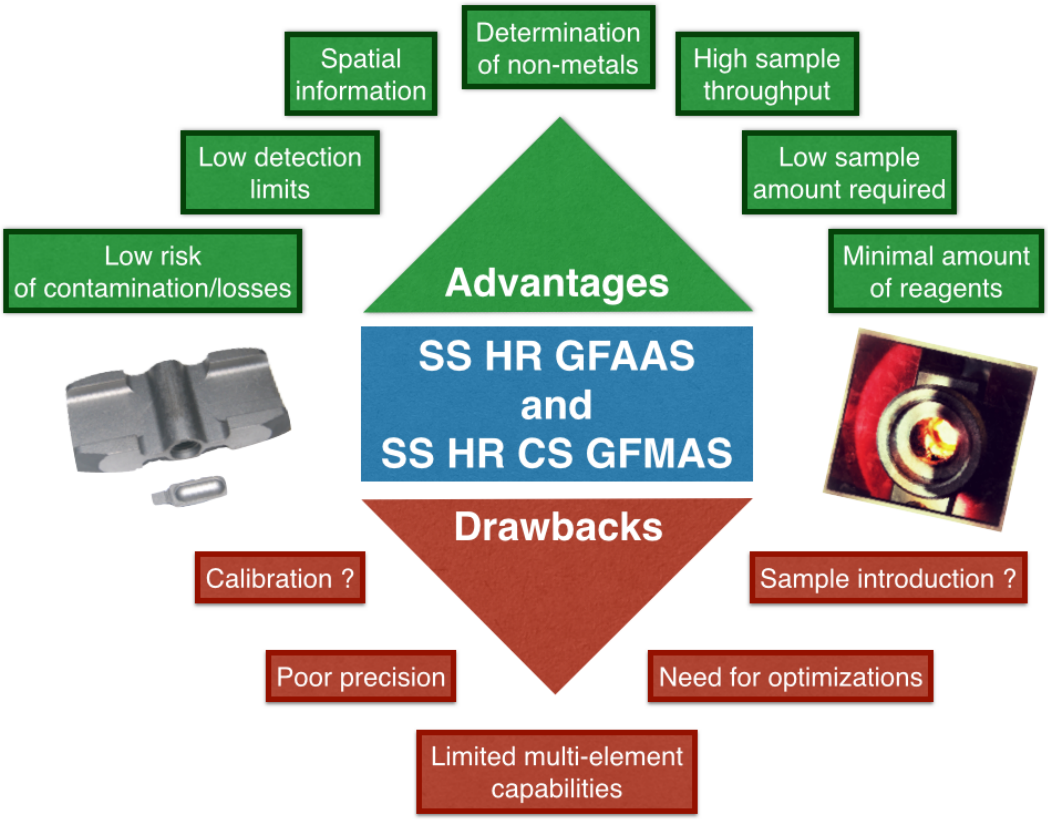

Figure 4

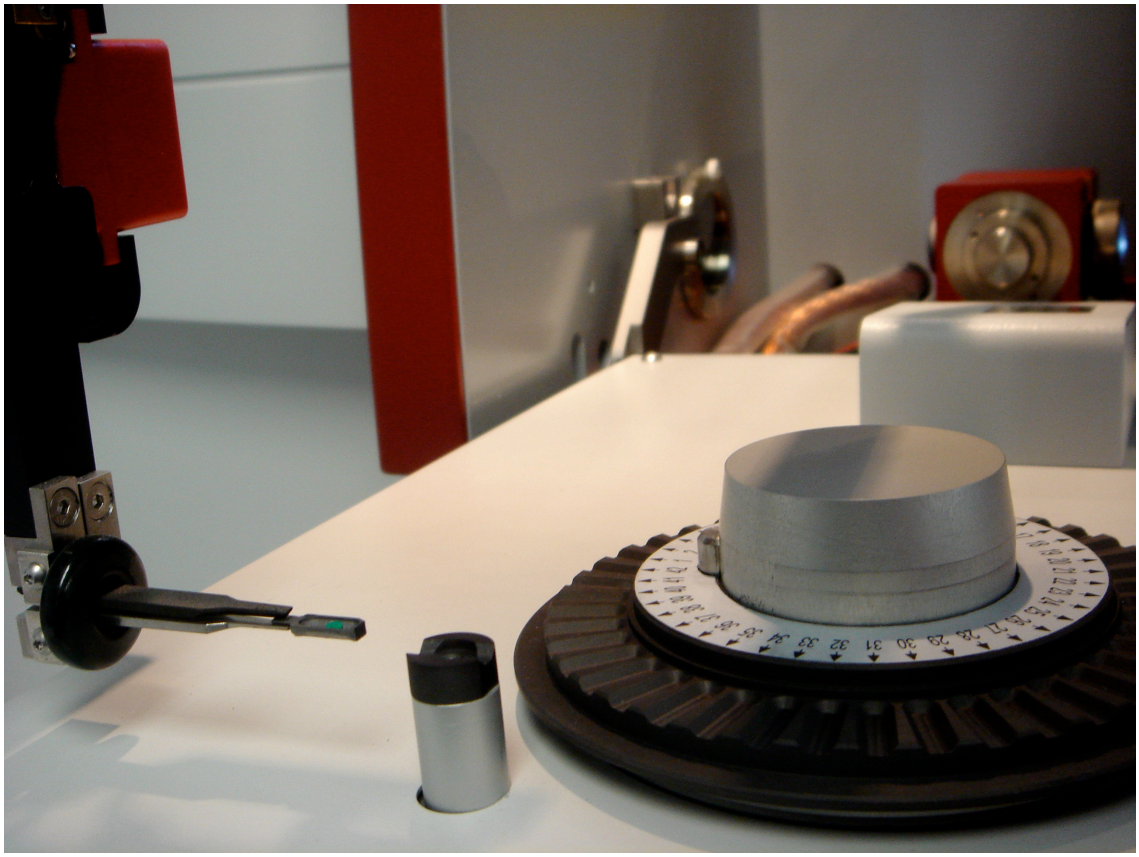

Figure 5

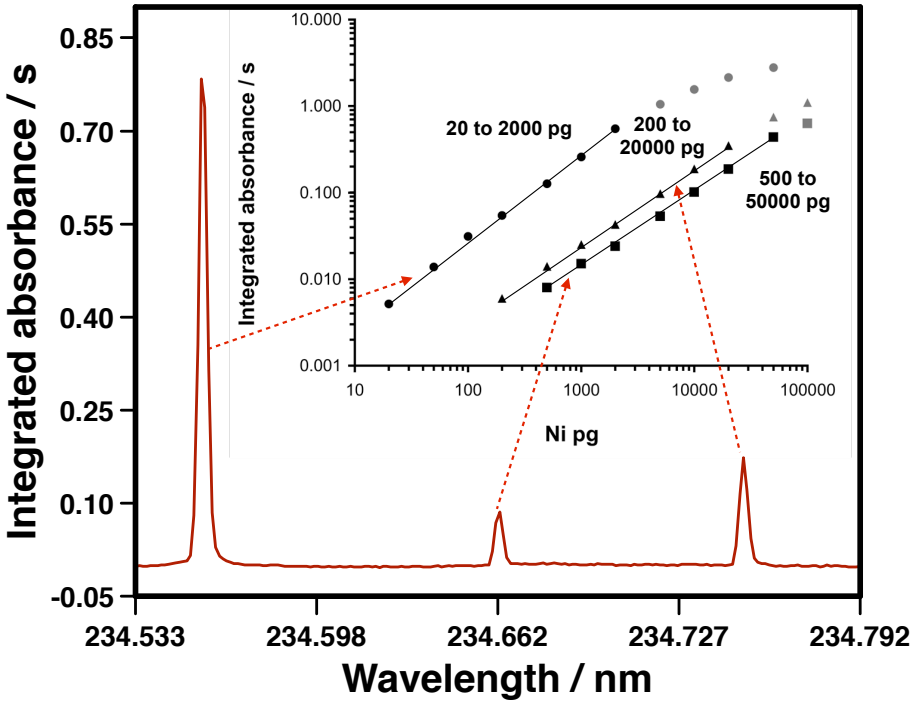

Figure 6

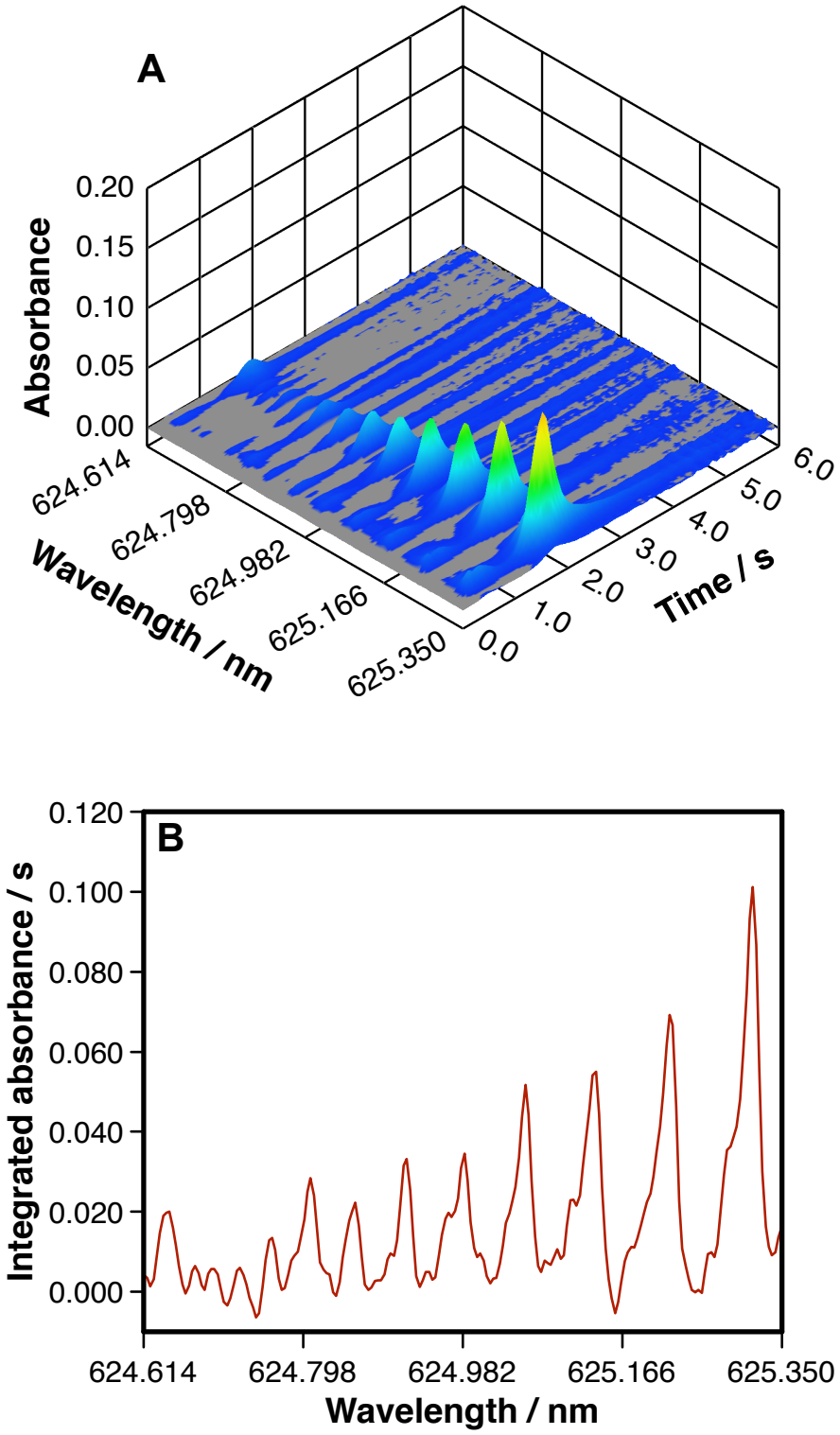

Figure 7

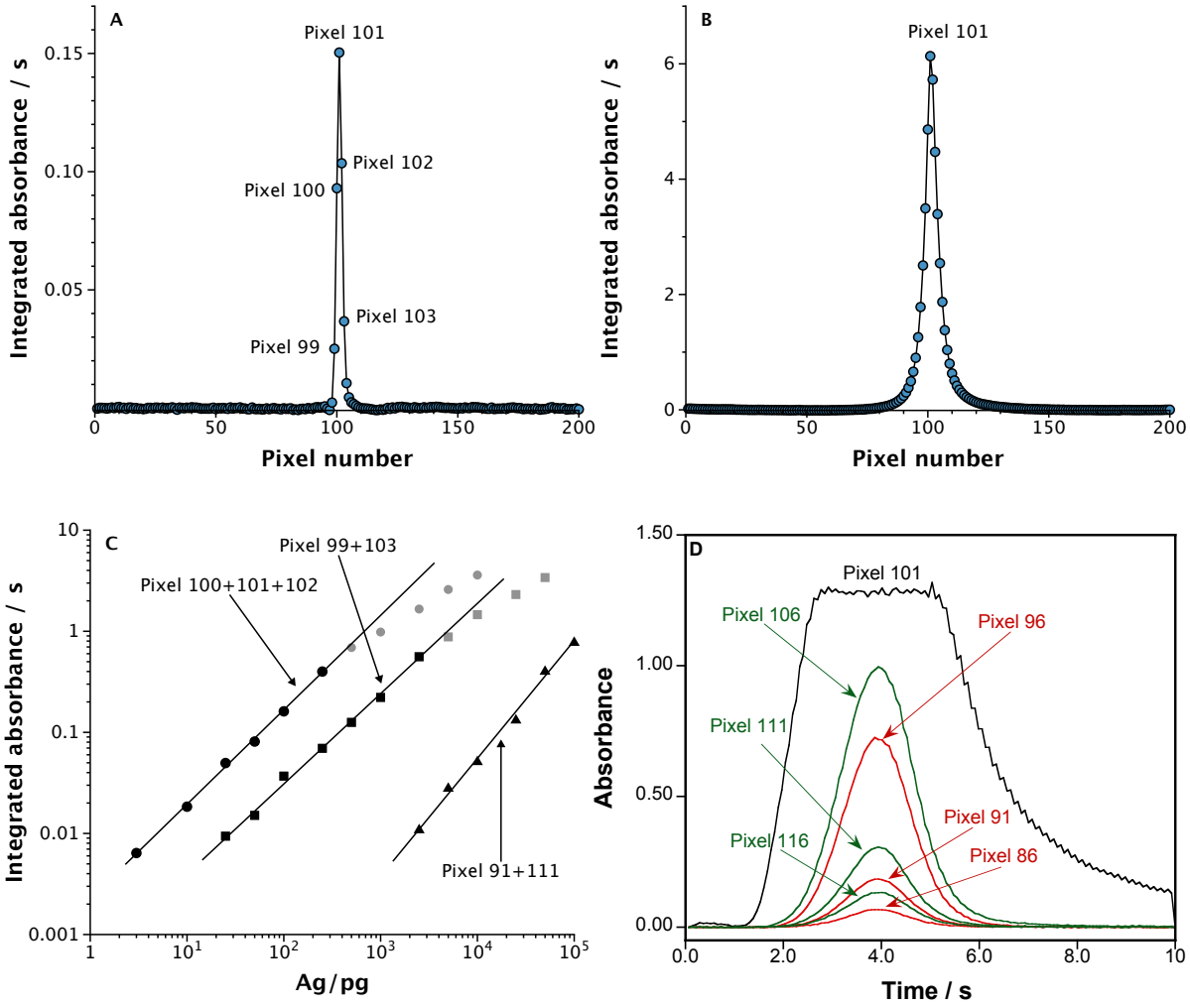

Figure 8

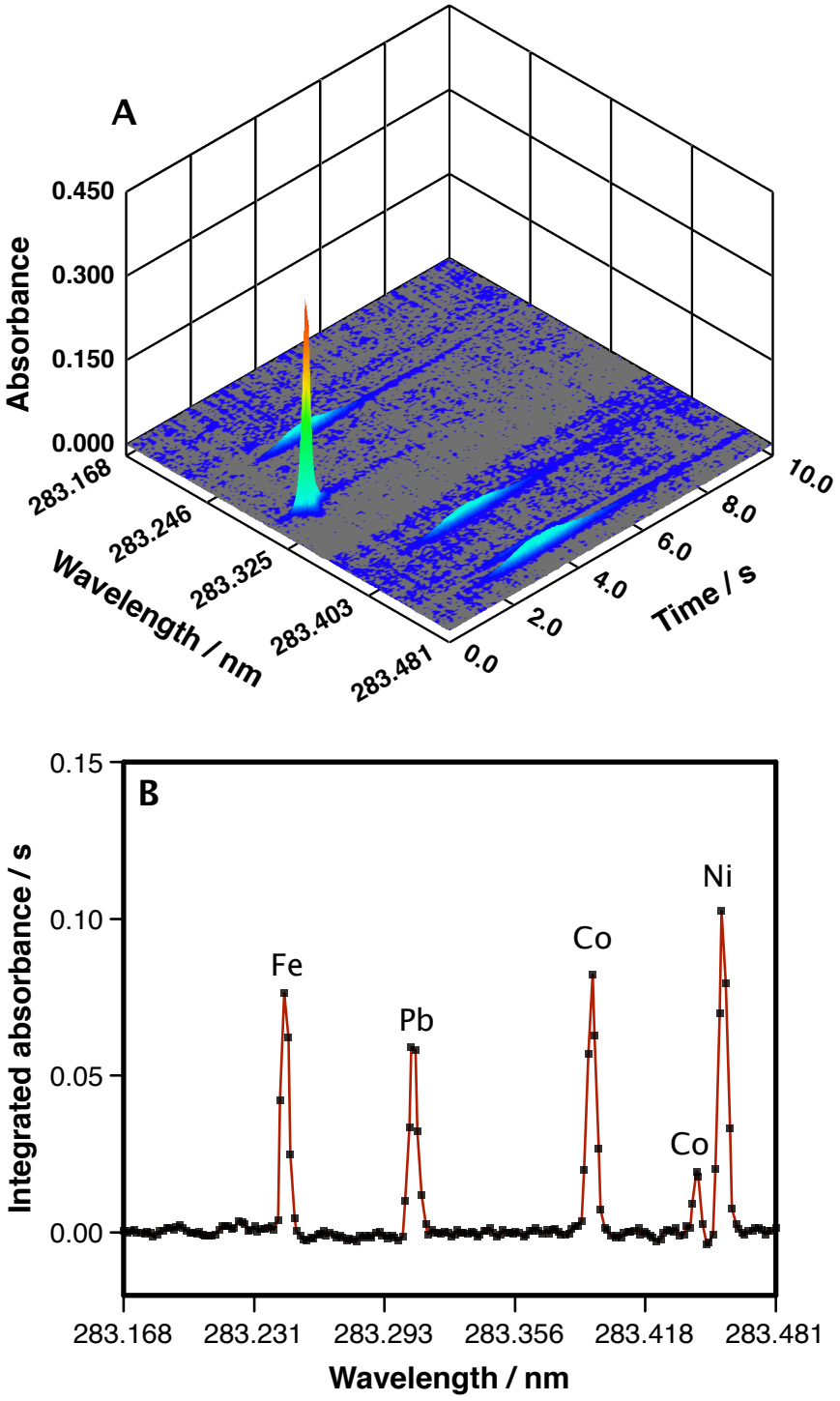

Figure 9

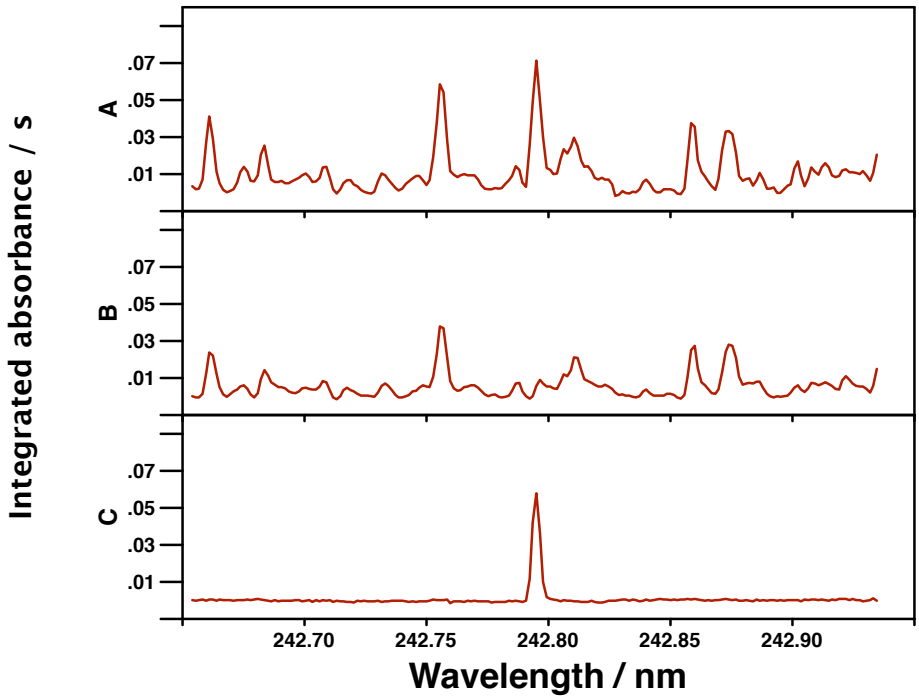

Figure 10

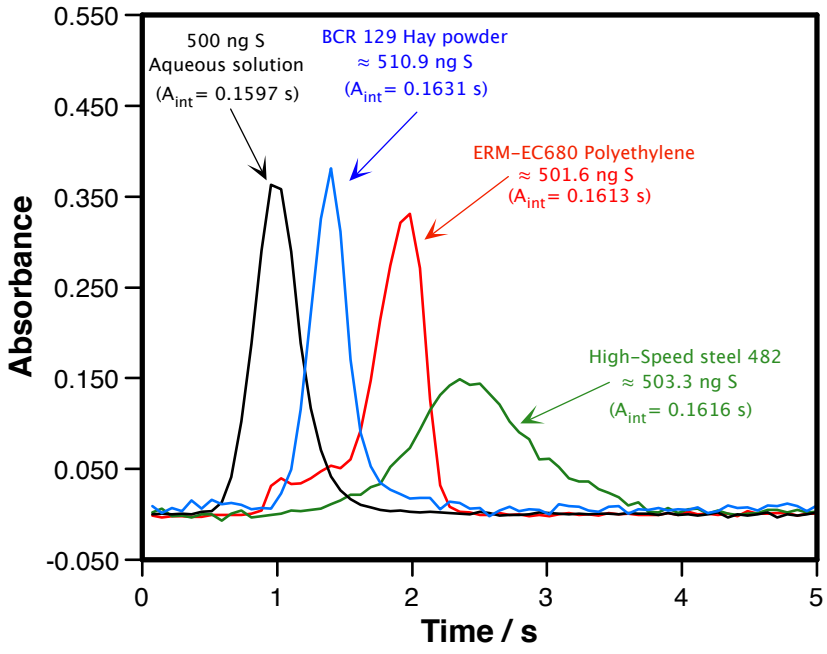

Figure 11

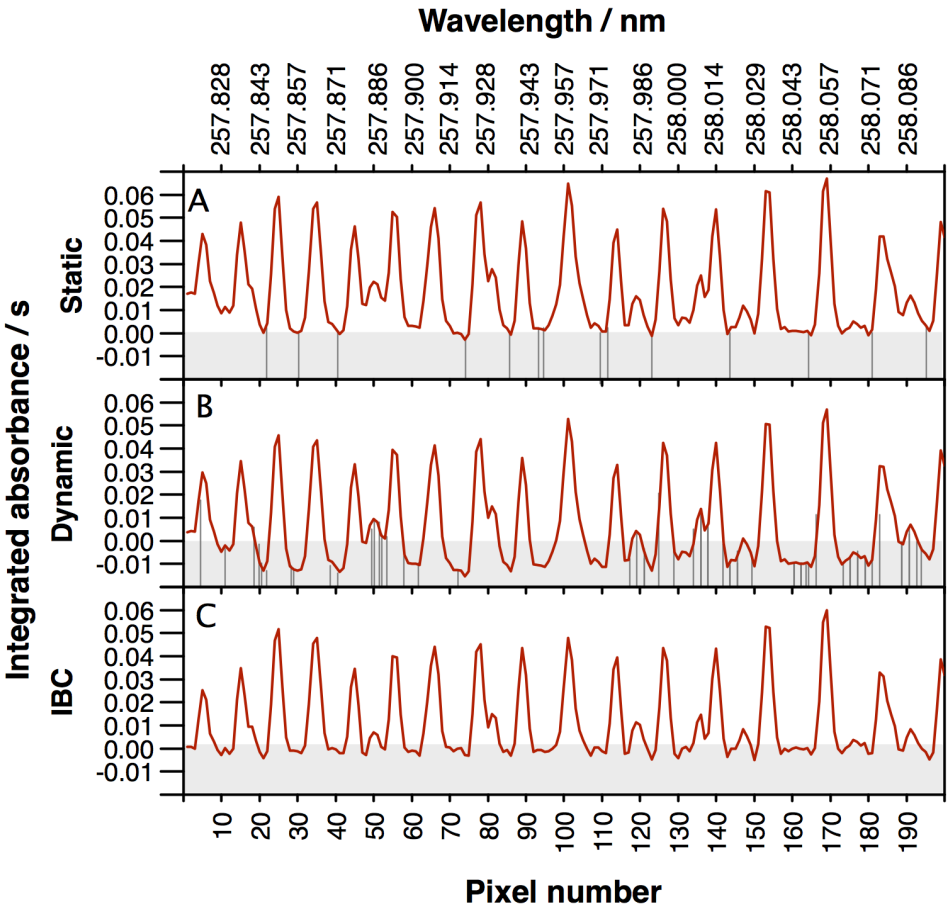

Table 1. Articles reporting on the use of HR CS GFAAS for the direct analysis of metals, chemicals and materials.

Analyte (Species monitored)	λ (nm)	LOD / m_0	Chemical modifier or reagent	Sample	Remark	Ref.
Br (as CaBr)	4 lines in the vicinity of 625.315	1.8 μg·g^{-1}/1.32 ng	Pd + Ca	Polymeric CRMs	Monitoring various lines serves to decrease LOD and to adjust the sensitivity to the analyte content Use of side pixels for the latter purpose is not recommended due to the dissymmetry of the peaks Aqueous standards for calibration	55
Br (as CaBr)	625.315	1.5 μg·g^{-1}/3.4 ng	Zr (permanent modifier) + Ca	Coal CRMs	The reagent (Ca) and the sample were separated (one deposited onto the graphite tube, the other onto the platform) for investigating the mechanism of formation CaBr Aqueous standards for calibration	81
Cd	228.802	2 ng·g^{-1}/0.4 pg	Ir (permanent modifier)	Coal	Evaluation of the influence of sample mass on precision Aqueous standards for calibration	47
Cd	228.802	0.6 ng·g^{-1}/1.0 pg	Ir, Ru (permanent modifiers, alone or with W) or Pd+Mg	Coal CRMs and samples	Slurry sampling Comparison of LS GFAAS and CS GFAAS. Use of CS- for diagnostics. Cd losses are observed for some samples that cannot be avoided by using any modifier combination.	84
Co **V**	240.725 240.674	8 μg·kg^{-1}/7.2 pg 1.2 mg·kg^{-1}/2.1 ng	Pd + Triton X-100	Crude oil CRMs and real samples	Simultaneous determination of Co and V using compromise atomization conditions Use of side pixels to adjust Co sensitivity to the analyte content Aqueous standards for calibration	59
Co **Co** **Fe** **Ni** **Pb**	283.393 283.443 283.245 283.445 283.306	86 ng/82 ng 440 ng/400 ng 6 ng/18 ng 65 ng/66 ng 23 pg/17 pg	Pd	Carbon nanotubes	Simultaneous determination using compromise conditions Use of side pixels to adjust sensitivity to the analyte content Evaluation of sample homogeneity Aqueous standards for calibration	35
Cr **Fe**	357.868 358.120	1μg·kg^{-1}/3.6 pg 0.6 mg·kg^{-1}/0.5 ng	No modifier	Crude oil CRMs and samples	Simultaneous determination of Cr and Fe. Direct analysis of the oils is preferred over emulsification Aqueous standards for calibration	94
Cr **Cu**	357.869 324.754	0.05 mg·kg^{-1}/4.8 pg 0.03 mg·kg^{-1}/3.2 pg	No modifier	Activated charcoal and	Separate determinations of the analytes Use of LSBC for subtraction of the molecular absorption	53

Fe **Fe** **Mn** **Mo** **Ni** **Ni** **V**	344.099/ 344.388 403.076 313.259 232.003/ 232.138 318.540	0.9 mg·kg^{-1}/240 pg --/890 pg 0.03 mg·kg^{-1}/5.5 pg 0.04 mg·kg^{-1}/7.0 pg 0.006 mg·kg^{-1}/25 pg --/162 pg 0.01 mg·kg^{-1}/26 pg		carbon black for Lyocell fiber production	due to SiO (Ni determination) or to a S-based species (V determination) For Fe and Ni two lines are simultaneously monitored to adjust the sensitivity Aqueous standards for calibration for Cu, Fe, Mo and Ni, but for V, Cr and Mn, matrix matched standards are needed	
Cr **Sb**	357.869 231.147	0.06 mg·kg^{-1}/62 pg 0.06 mg·kg^{-1}/35 pg	No modifier for Cr. Pd+Mg+Triton X-100 for Sb	Polymers	Separate determinations of the analytes Aqueous standards for calibration	91
F (as CaF)	606.44	5 mg·kg^{-1}/0.1 ng	Zr (permanent modifier) + Ca	Niobium oxide (Nb_2O_5)	Slurry sampling CaF molecule is used instead of GaF (more sensitive) due to the high F contents expected The order of addition of modifier/reagent is important to ensure CaF formation Calibration by means of standard additions	86
Hg	253.652	0.6 µg·g^{-1}/1.5 ng	No modifier for the solid samples	Polymeric CRMs	Lower LODs, broader linear range, better sensitivity and superior performance for BG correction observed for HR CS GFAAS, in comparison with LS GFAAS Aqueous standards for calibration	30
P	213.618	0.5 µg·g^{-1}/ 5 ng	Pd + Mg	Biodiesel (undiluted)	Importance of using a multi-step drying procedure Calibration with organic matrix-matched standards	98
Pb	217.001	0.008 µg·g^{-1}/5 pg	No modifier	Coal CRMs	HR CS GFAAS enables the monitoring of potential interferences as a function of the atomization temperature Aqueous standards for calibration	68
Pb	283.306	21.3 pg/12.6 pg	No modifier	Lipsticks	Investigation of the effect of sample mass Aqueous standards for calibration	44
Pb	217.000	0.005 µg·g^{-1}/13.2 pg	Pd	Lipsticks and their raw materials (TiO_2, zeolites, mica, silica, etc.)	283.306 nm line used to decrease sensitivity Aqueous standards for calibration	99
S (as CS)	Sum of 6 lines in the vicinity of	1 µg·g^{-1}/3 ng	Ru (permanent modifier) + Pd nanoparticles	CRMs of very different matrix compositions (polyethylene,	The use of Pd nanoparticles as chemical modifier permits to obtain a similar sensitivity for different S species and different sample matrices Summing 6 lines for the CS system reduces LODs and m_0	78

	258 nm			steel, hay, oyster tissue and coke)	values significantly. Lines have to be selected carefully for avoiding overlaps with Fe and Co signals. Aqueous standards for calibration	
S (as CS)	258.033	0.03 µg/--	Ru (permanent modifier)	Coal CRMs and real samples	A two-peak signal is obtained for coal, probably due to the presence of different S species (organic and inorganic). Aqueous standards for calibration, but the chemical compound selected for preparing them is important. L-cysteine provides satisfactory results	79
S (as CS)	257.592	0.01% (w/w)/--	HNO_3 +Triton X-100	Coal and coal fly ash CRMs	Slurry sampling Peak height used for signal evaluation as it provides better RSD% and linearity Aqueous standards for calibration	85
Tl	276.787	0.01 $\mu g \cdot g^{-1}$/5.5 pg	No modifier	Coal CRMs and real samples	Interfering species can be separated in time Comparison with LS GFAAS Aqueous standards for calibration	83

Table 2. Articles reporting on the use of HR CS GFAAS for the direct analysis of clinical and biological materials, foods and beverages.

Analyte (Species monitored)	λ (nm)	LOD / m_0	Chemical modifier or reagent	Sample	Remark	Ref.
Ag	328.068	0.7 pg/--	Pd nanoparticles	*Daphnia magna* specimens exposed to Ag nanoparticles	Direct determination of the Ag body burden in individual specimens of *Daphnia magna* exposed to Ag nanoparticles Use of side pixels to adjust sensitivity to the analyte content Aqueous standards for calibration with Ag in ionic form	37
Ag nano-particles	328.068	--	No modifier	Parsley	A new evaluation strategy (based on the study of the atomization delay and the atomization rate) was developed for distinguishing between ionic silver and silver nanoparticles directly in solid samples. Possibility for sizing Ag nanoparticles is also demonstrated.	88
Al (as AlF)	227.477	1.8 $\mu g \cdot L^{-1}$/0.5 $\mu g \cdot L^{-1}$	$NH_4F \cdot HF$	Blood samples	Addition of $NH_4F \cdot HF$ permits the formation of AlF and favors matrix removal, minimizing matrix effects Use of LSBC for subtraction of the molecular absorption due to N-based species Aqueous standards for calibration	96
As **Cd** **Cu** **Cr** **Fe** **Mn** **Pb** **Se**	193.696 228.802 324.754 357.869 248.327 279.482 283.306 196.027	0.080 $\mu g \cdot g^{-1}$/-- 0.002 $\mu g \cdot g^{-1}$/-- 0.004 $\mu g \cdot g^{-1}$/-- 0.005 $\mu g \cdot g^{-1}$/-- 0.010 $\mu g \cdot g^{-1}$/-- 0.002 $\mu g \cdot g^{-1}$/-- 0.007 $\mu g \cdot g^{-1}$/-- 0.060 $\mu g \cdot g^{-1}$/--	HNO_3 and Triton X-100 plus Pd, Pd+Mg, Mg or $NH_4H_2PO_4$	Multivitamin dietary supplements. Animal and vegetal tissue CRMs	Slurry sampling Separate determinations of the analytes Calibration by means of standard additions	92
Au	242.795 267.595	2 $ng \cdot g^{-1}$/7.5 pg -- / 16.6 pg	Pd	Mice tissues	Monitoring of Au nanoparticle distribution in various mice organs Use of LSBC for sequential subtraction of the molecular absorption due to PO Calibration with aqueous standards with Au in ionic form	72
Cd	228.802	0.6 $\mu g \cdot kg^{-1}$/0.9 pg	W + Ir (permanent	Grain products	Use of the main Cd line and of a secondary Fe line that can	93

Fe	228.726	0.5 mg·kg^{-1}/1.2 ng	modifiers)		be simultaneously monitored Sequential determination using two atomization temperatures (1700º C for Cd, 2600 ºC for Fe) Aqueous standards for calibration	
Cd **Fe**	228.802 228.726	2.0 µg·kg^{-1} /0.7 pg 4.5 mg·kg^{-1} /1.0 ng	W + Ir (permanent modifiers)	Bean and soil samples	Application of the method developed in ref. 93 to new types of samples. Use of side pixels to adjust Fe sensitivity to the analyte content Aqueous standards for calibration	60
Co	240.725	5 ng·g^{-1}/--	No modifier	Biological CRMs (animal tissues and human hair)	Comparison with LS GFAAS. A four-fold LOD improvement observed for HR CS GFAAS Aqueous standards for calibration	70
Co **Fe** **Fe** **Ni**	352.685 352.604 352.617 352.454	--/75 pg --/3 ng --/27 ng --/30 pg	Pd	NIST SRM 1566a Oyster tissue	Simultaneous determination Aqueous standards for calibration	52
Cd **Ni** **Ni**	228.802 228.998 234.554	 11 pg/16 pg	Pd	BCR CRM 679 White cabbage	Comparison between truly simultaneous (228.802 nm and 228.998 nm) or sequential (228.802 nm and 234.554 nm) monitoring of Cd and Ni from the same sample aliquot Aqueous standards for calibration	
Cr	357.869	3.0 ng·g^{-1}/5 pg	No modifier	Botanical CRMs and medicinal plants	Air assisted pyrolysis at 600ºC to avoid residues Evaluation of sample homogeneity Aqueous standards for calibration	61
Fe **Ni**	232.036 232.003	0.40 µg·kg^{-1}/180 pg 25 µg·kg^{-1}/16 pg	No modifier	Pine needles and lichen	Simultaneous determination of Ni and Fe Use of LSBC for subtraction of the molecular absorption due to SiO Calibration with aqueous standards	74
Hg	253.652	0.1 µg·g^{-1}/17 pg	No modifier for the solid samples	Biological CRMs (animal tissues and human hair)	Addition of $KMnO_4$ needed only for aqueous standards, to prevent Hg losses Aqueous standards for calibration	66
Mo **Ti**	319.397 319.200	1.5 µg·L^{-1}/1.6 µg·L^{-1} 6.5 µg·L^{-1}/6.6 µg·L^{-1}	Pt	Urine in clinical filter paper	Simultaneous determination Direct solid sampling of dried urine spots Matrix-matched standards for calibration	95
Ni	228.999	8.3 pg/--	No modifier	*Daphnia magna* specimens	Direct determination of the Ni body burden in individual specimens of *Daphnia magna*	100, 101

					Aqueous standards for calibration	
P	213.618	5 μg·g^{-1}/4.6 ng	W (permanent modifier)+ ascorbic acid + Pd	Biological CRMs (vegetal and animal tissue)	Comparison of advantages and drawbacks when monitoring either P or PO Aqueous standards for calibration	57
P (as PO)	Sum of 9 lines in the vicinity of 213.561	20 μg g^{-1}/4.7 ng	W (permanent modifier)			
Pb	217.001	0.01 μg·g^{-1}/5.6 pg	Ru (permanent modifier)	Biological CRMs (hair, animal tissue and blood)	Use of the most sensitive Pb line made possible due to enhanced BG correction. Use of LSBC for subtraction of the molecular absorption due to PO Aqueous standards for calibration	71
Pb	283.306	7.2 ng·g^{-1}/12 pg	Pd	Medicinal plants	Air assisted pyrolysis at 600ºC to avoid residues Aqueous standards for calibration	46
Pb	283.306	0.82 ng·g^{-1}/--	$NH_4H_2PO_4$	Human hair CRMs and real samples	Investigation of Pb distribution in the samples Aqueous standards for calibration	102
Pb	283.306	2.3 μg·kg^{-1}/8.1 pg	No modifier	Rice grains	The method is used for studying the homogeneity of single rice grains Aqueous standards for calibration	62
S (as CS)	258.033	15 ng/18 ng	W (permanent modifier) + Pd	Biological CRMs (botanical samples and milk)	Aqueous standards for calibration, but the chemical compound selected for preparing them is important. Thiourea provides satisfactory results	77
S (as CS)	258.056	3.5 ng/8.1 ng	Ir (permanent modifier) + Pd nitrate	Food samples	Study of sample homogeneity Aqueous standards for calibration	80
Zn	307.590	1.4 ng /2.5 ng	No modifier	*Daphnia magna* specimens	Direct determination of the Zn body burden in individual specimens of *Daphnia magna* Use of side pixels used to adjust sensitivity to the analyte content Aqueous standards for calibration	36

Table 3. Articles reporting on the use of HR CS GFAAS for the direct analysis of environmental samples.

Analyte (Species monitored)	λ (nm)	LOD / m_0	Chemical modifier or reagent	Sample	Remark	Ref.
Ag	328.068	2 ng·g^{-1}/--	No modifier	Geological CRMs (soil, sediments, rocks and ores)	Use of LSBC for subtraction of the molecular absorption due to SO_2 Aqueous standards for calibration for soils and sediments For rocks and ores, calibration with matrix matched solid standards is required due to the occurrence of gas phase interferences	73
Ag	338.289	17 ng·g^{-1}/4.4 pg	Ru (permanent modifier)	Airborne particulate matter on glass fiber filters	Investigation of the effect of sample mass Aqueous standards for calibration	103
Cd **Fe**	228.802 228.725	0.03 µg·g^{-1}/0.9 pg 90 µg·g^{-1}/1.6 ng	HF + HNO_3	Sewage sludge CRMs and real samples	Slurry sampling Use of main Cd line and of secondary Fe line that can be simultaneously monitored Sequential determination using two atomization temperatures (1300º C for Cd, 2300 ºC for Fe) Aqueous standards for calibration	67
Cd	228.802	7.5 ng·g^{-1}/1.0 pg	Ir (permanent modifier) or Pd+Mg	Fertilizer CRMs and real samples	Slurry sampling Use of Pd+Mg preferred over Ir modifier, as the latter provides results biased low Aqueous standards for calibration	104
Cd **Cr** **Cr**	228.802 357.869 428.972	1.1 µg·kg^{-1}/0.4 pg 21 µg·kg^{-1}/2.5 pg 90 µg·kg^{-1}/72 pg	No modifier	Biomass samples and their ashes	Sequential determination from the same sample aliquot Determination using two atomization temperatures (1500º C for Cd, 2600 ºC for Cr) and a different wavelength for each element Aqueous standards for calibration	75
Cu **Cu** **Mo** **Sb**	324.754 216.509 313.259 212.739	15 µg·g^{-1}/-- 15 µg·g^{-1}/-- 15 µg·g^{-1}/--	Ru (permanent modifier) for Sb. No modifier for Cu and Sb.	Airborne particulate matter on glass fiber filters	Separate determinations of the analytes Comparison of three different methods: solid sampling, MW-assisted acid leaching and ultrasound acid extraction. Two different lines measured for Cu in order to adjust sensitivity to the analyte content Aqueous standards for calibration	89

Hg	253.652	40 ng·g^{-1}/22 pg	$KMnO_4$	Airborne particulate matter on glass fiber filters	Very similar conditions can be used for Hg in different matrices (polymers, biological tissues, glass filters) Aqueous standards for calibration	105
Mo **Sb**	313.259 217.582	15 µg·g^{-1}/28 pg 15 µg·g^{-1}/38 pg	Ru (permanent modifier) for Sb. No modifier for Mo	Cairo's dust collected from tree leaves	Separate determinations of the analytes Aqueous standards for calibration	90
Pd	244.791	0.7 pg·m^{-3}/0.21 pg	No modifier	Airborne particulate matter on quartz fiber filters	Effect of sample mass evaluated Use of a solid standard (Road dust CRM) for calibration	43
Sb	231.147	0.02 µg·kg^{-1}/ 28 pg	Ir (permanent modifier)	Sediment CRMs	Use of LSBC for sequential subtraction of the molecular absorption due to SiO and PO Aqueous standards for calibration	40
Sb	212.739	15 µg·g^{-1}/0.7 ng	Ru (permanent modifier)	Airborne particulate matter on glass filters	Investigation of the effect of sample mass Aqueous standards for calibration	51
Se	196.026	30 ng·g^{-1}/50 pg	Ru (permanent modifier) + Ru solutions	Soil CRMs and real samples	Use of LSBC for sequential subtraction of the molecular absorption due to NO and PO Aqueous standards for calibration	97
Tl	276.787	0.02 µg·g^{-1}/15-16 pg	No modifier is needed for HR CS AAS	Marine sediment CRMs	Surry sampling Use of LSBC for subtraction of the molecular absorption due to SO_2 Comparison with Zeeman LS GFAAS Aqueous standards for calibration	18