



# Determination of chlorine via the CaCl molecule by high-resolution continuum source graphite furnace molecular absorption spectrometry and direct solid sample analysis

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## ARTICLE INFO

### Keywords:

Solid sample analysis  
High-resolution continuum source molecular absorption spectrometry  
Chlorine determination  
CaCl molecular absorption

## ABSTRACT

This work investigates the possibilities of high-resolution continuum source graphite furnace molecular absorption spectrometry for the direct determination of Cl in solid samples via the CaCl molecule and measurement of its molecular absorption. The method proposed is based on addition of 400 µg Ca as molecule-forming reagent and of 20 µg Pd as chemical modifier, which helps to stabilize the analyte and enhances sensitivity.

The molecular spectrum for CaCl offers different lines with different limits of detection and linear ranges, which permitted to analyze solid samples with different Cl contents. The lowest limit of detection (0.75 ng Cl, corresponding to 0.75 µg g<sup>-1</sup> for a typical sample mass of 1 mg) could be achieved by combination of three of the most sensitive lines in the vicinity of 620.862 nm, while the amplest linear range (up to 860 ng Cl) was achieved by selection of the less sensitive line at 377.501 nm.

The method developed enabled the direct determination of Cl in solid samples using simple external calibration with aqueous standards. Good precision (5–9% RSD) and accuracy was attained in a series of certified samples of very different nature (i.e. coal, iron oxide, polyethylene, human hair, pine needles, rice flour and milk) and with very different Cl contents, ranging from about 50 µg g<sup>-1</sup> to 1% (w/w) Cl. The method appears as particularly useful for Cl determination in samples with elevated Ca contents, for which biased results with other diatomic molecules, such as AlCl or SrCl, may be obtained.

## 1. Introduction

Chlorine (Cl) is relatively abundant in the Earth's crust (0.0314% w/w), where is found in the bound state only and mainly as common salt (NaCl). This compound is one of the most abundant and easy to transform raw material on earth, and is the basis of a vast number of applications of the chlorine chemistry family: products for drinking water sanitation, paper products, dyestuffs, textiles, petroleum products, medicines, antiseptics, insecticides, foodstuffs, solvents, paints, plastics, among many other consumer products and industrial applications [1,2].

Concerning toxicity, chlorine is essential to all known species of life in the form of chloride ions, while in other chemical forms the effects of this element and its compounds range from inert to highly toxic [1]. As a result of all of the above, and given the extensive presence of chlorine

and its derivatives in everyday life, determination of trace levels of this element in a wide variety of samples is important in many contexts.

Besides the classical methods for determination of chloride ions such as gravimetric, volumetric or colorimetric methods, chlorine determination in different samples and chemical forms can be accomplished by a variety of analytical techniques including potentiometry, total reflection X-ray fluorescence, neutron activation analysis or inductively coupled plasma mass/optical emission spectrometry [3]. When aiming at analyzing solid samples, however, most of these analytical techniques generally require extensive sample treatment before analysis [4], which involves high risk of analyte losses and/or contamination and require longer analysis times. In these situations, the use of direct solid sample analysis could help overcoming these problems [5–7].

Among techniques for direct solid sample analysis, graphite furnace

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atomic absorption spectrometry (GFAAS) is an attractive and versatile alternative providing high sensitivity at a reasonable cost [5–7]. However, chlorine has been traditionally inaccessible for this technique since the analytical lines for this element lie in the vacuum ultraviolet, not available for conventional AAS spectrometers.

This situation changed substantially after the commercial introduction of high-resolution continuum source atomic absorption spectrometry (HR-CS AAS) in the last decade [8]. Among other advantages, the introduction of this technique opened the possibility for the determination of non-metals (including chlorine) via the formation of diatomic molecules in the graphite furnace and subsequent measurement of their molecular absorption at any wavelength lying in the spectral range provided by the continuum source used in these instruments (189–900 nm for a Xe short-arc lamp) [9–11]. Such strategy had been already tested in the past for chlorine determination, and the monitoring of the molecular absorption corresponding to different monochlorides (namely AlCl, GaCl or InCl) using conventional AA spectrometers [12–16] was explored. However, the low resolution of the spectrometers available at the time resulted in many problems for these determinations.

With the introduction of high-resolution continuum source instruments these problems were overcome and the determination of non-metals via molecular absorption spectrometry (MAS) was made possible for routine analytical laboratories. Since that moment, a few papers have been published exploring this possibility for chlorine determination, mostly in graphite furnaces, and based on the formation and measurement of AlCl [17–19], InCl [19] or SrCl [19–21]. The latter molecule was introduced only very recently by Pereira et al. [20] and its use has allowed the development of the only two direct solid sample analysis approaches available to date based on HR-CS GFMAAS, aiming at Cl determination in biological samples [20] or coal [21], respectively.

The preferential use of these molecules for Cl determination via HR-CS MAS is based on different reasons. Compared to atomic absorption spectrometry (AAS), MAS has the disadvantage of being more prone to both spectral and, particularly, non-spectral interferences. HR-CS MAS does not simply require the atomization of the analyte, but it necessitates the formation of analyte molecules with other species that need to be stable at the high temperatures of the graphite furnace, even in the potential presence of concomitants. These concomitants, if highly concentrated in the samples (which can be particularly problematic in the case of direct solid sample analysis), might compete for the analyte. As a result, molecules with elevated bond dissociation energy are usually selected for HR-CS MAS in order to favor their formation and stability in the graphite furnace.

With a bond dissociation energy of  $511 \text{ kJ mol}^{-1}$  [2], AlCl is one of the strongest monochlorides and, therefore, it is not surprising that the first papers published for Cl determination by HR-CS GFMAAS were based on the formation of the AlCl molecule [17,18]. SrCl, on the other hand, presents a lower bond dissociation energy ( $406 \pm 13 \text{ kJ mol}^{-1}$ ) [2] but offers high sensitivity for Cl determination by HR-CS GFMAAS as well. Moreover, this molecule shows the advantage that its main band is considerably narrower than that of AlCl, and it lies in a spectral range where the risk for spectral overlap is also considerably lower (261.42 nm for AlCl vs. 635.862 nm for SrCl). This is why the most recent papers have been published based on the formation of this molecule [19–21], permitting to avoid, e.g., Co spectral overlap with the band of the AlCl molecule at 261.42 nm.

Unfortunately, and even after carefully selecting the target molecule according to the parameters described, complete absence of non-spectral interferences cannot be assured for HR-CS GFAAS if concomitants being able to form other strong chemical species with the analyte are present at high concentrations in the samples. Self-evidently, this fact limits applicability of the technique in some particular situations. In this sense, for instance, in a recent paper by our research group [22], Ca was found to significantly interfere in the

determination of Cl in hard water samples by means of HR-CS GFMAAS after formation of the AlCl molecule. In fact, although CaCl has a lower bond dissociation energy ( $409 \pm 8.7 \text{ kJ mol}^{-1}$ ) [2] than AlCl, the massive presence of Ca ions in hard water samples probably results in a significant population of Ca atoms in the gas phase competing for the chlorine atoms, thus reducing yield for the AlCl molecule. As a consequence, analytical results were significantly affected for samples presenting Ca/Cl ratios well above unity, when simple calibration with aqueous standards was attempted. For overcoming this problem, the use of isotope dilution for calibration proved successful, taking advantage of the fact that  $\text{Al}^{35}\text{Cl}$  and  $\text{Al}^{37}\text{Cl}$  absorb at slightly different wavelengths and, hence, chlorine isotope ratios can be accurately measured [22].

The problem of Ca interference cannot be considered as trivial, as this element is present at high concentrations in a wide variety of samples commonly analyzed for Cl (e.g. foodstuff like dairy products, vegetal samples, etc.), while the strategy based on the use of isotope dilution for solving the problem is not as straightforward and might not be suitable for use in routine labs. The alternative use of SrCl, on the other hand, is not probably solving the problem either (as will be shown in this work for different samples naturally showing elevated Ca contents), as this molecule has a weaker bond dissociation energy than AlCl and is bound to be affected by this interference in a similar way. Given the circumstances, it is worthwhile to explore new diatomic molecules for the determination of chlorine in this kind of samples. In fact, investigating CaCl, and therefore taking advantage of the element at the origin of the interference as counter ion, seems to be an interesting option.

In this context, this work explores for the first time the use of the CaCl molecule to determine Cl at trace levels by means of solid sample analysis with HR-CS GFMAAS. As previously mentioned, this molecule has a relatively high bond dissociation energy (similar to that of SrCl), and also presents several line-like transitions with different sensitivities located in the near UV and visible regions of the spectrum (around 377 nm and 618–620 nm), where the potential risk for spectral overlap is also minimized. Besides temperature program optimization, selection of adequate chemical modifiers and evaluation of figures of merit, analysis of reference materials of various nature, some of them containing high amounts of Ca in their composition, will be conducted for method validation. For comparison purposes, analysis of some of these samples by means of HR-CS GFAAS after formation of the SrCl molecule will be also carried out.

## 2. Experimental

### 2.1. Instrumentation

All molecular absorption measurements were conducted with a high-resolution continuum source absorption atomic spectrometer, the ContrAA 700, commercially available from Analytik Jena AG (Jena, Germany). The optical system comprises a xenon short-arc lamp (GLE, Berlin, Germany) operating in “hot-spot” mode as the radiation source. It also includes a double monochromator with a prism premonochromator, a high-resolution echelle grating monochromator and a charge-coupled device (CCD) array detector with 588 pixels, 200 of which are used for analytic purposes, while the rest are used for internal functions of the instrument. More details on this instrumental configuration can be found elsewhere [8]. This instrument is equipped with a transversely heated graphite tube atomizer. As additional accessories, the instrument is also equipped with an automated accessory (SSA 600) enabling the introduction of solid samples, which includes a microbalance (Sartorius M2P, Gottingen, Germany) with a precision of 0.001 mg. Pyrolytic graphite tubes and platforms designed for the direct analysis of solid samples were used throughout the study.

## 2.2. Reagents, standards and certified reference materials

High-purity water (Trace Select Ultra, Cl level lower than  $1 \mu\text{g kg}^{-1}$ , Fluka, Buchs, Switzerland) was used for the preparation of all solutions, while the rest of chemicals employed were of analytical grade or better. Cl standards were prepared by proper dilution of a  $1000 \text{ mg L}^{-1}$  chloride stock solution (NaCl in water, Darmstadt, Merck, Germany). A  $40 \text{ g L}^{-1}$  Ca solution was prepared by dissolving appropriate amounts of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (Merck, Germany) in high purity water and was used as the molecule-forming solution to generate CaCl. For the comparative measurements based on formation of the SrCl molecule, the molecule-forming solution was prepared by dissolving appropriate amounts of  $\text{Sr}(\text{NO}_3)_2$  (Merck) in high purity water up to a concentration of  $10 \text{ g L}^{-1}\text{Sr}$ . In both cases, Pd (as nitrate) was used as chemical modifier. Modifier solutions were prepared from a stock

standard Pd solution of  $10 \text{ g L}^{-1}$  ( $\text{Pd}(\text{NO}_3)_2$  in  $15\% \text{ HNO}_3$ , Merck) that was properly diluted to a concentration of  $2 \text{ g L}^{-1}$ . In the case of the SrCl molecule, moreover, Zr was also used as permanent chemical modifier and a  $1 \text{ g L}^{-1}$  Zr solution (Merck) was used for pretreating the sampling platforms as described in Section 2.3. Additionally, two Pd and Pt nanoparticles dispersions were tested as chemical modifiers. A  $1.8 \text{ g L}^{-1}$  20 nm Pd nanoparticle dispersion was prepared following the method described in a previous work [23], while a  $1.07 \text{ g L}^{-1}$  5 nm Pt nanoparticle dispersion (Citrate BioPure Platinum) was purchased from Nanocomposix (San Diego, USA).

Finally, eight certified reference materials (CRM) of very different nature, with certified Cl levels covering a wide range of concentrations at the minor and trace levels and, in some cases, showing a naturally occurring elevated Ca concentration were analyzed in this work: SRM 2692c Bituminous Coal, SRM 1575 Pine Needles, SRM 1568b Rice Flour and SRM 1549 Non-fat milk powder, all four available from NIST (National Institute of Standards and Technology, Gaithersburg, MD, USA); CRM BCR 460 Coal and CRM EC681 Polyethylene (European Commission, Joint Research Centre, Institute for Reference Materials and Measurements, Brussels, Belgium), CRM NCS ZC 81002b Human Hair (China National Analysis Centre for Iron and Steel, Beijing, China), and CRM 686-1  $\text{Fe}_2\text{O}_3$ , (European Committee for Iron and Steel Standardization, Düsseldorf, Germany). Some details for each material tested are gathered in Table 1.

**Table 1**

Certified reference materials analyzed in this work.

CRM reference	Type of sample	Certified Cl content / $\mu\text{g g}^{-1}$	Certified Ca content /% w/w
NCS ZC 81002b	Human Hair	48.2 <sup>a</sup>	$0.1537 \pm 0.0068$
CRM BCR 460	Coal	$59 \pm 18$	–
ERM EC681	Polyethylene	$92.9 \pm 2.8$	–
SRM 1575	Pine Needles	$293 \pm 20$	$0.41 \pm 0.02$
SRM 1568b	Rice Flour	$301.1 \pm 3.8$	$0.012 \pm 0.00031$
CRM 686-1	Iron Oxide	$950 \pm 60$	$0.0097 \pm 0.0007$
SRM 2692c	Bituminous Coal	$1338 \pm 22$	–
NIST SRM 1549	Non-fat milk powder	$10900 \pm 200$	$1.30 \pm 0.05$

<sup>a</sup> Informative value.

## 2.3. Procedure for analysis of the certified reference materials

Most CRMs were directly analyzed as solids by means of HR-CS SS-GFMA. Only SRM 1549 Non-fat milk powder was analyzed as an aqueous suspension due to its high Cl content. For preparing the suspension, 0.5 g of the solid sample were weighed in a polypropylene tube and volume was made up to 20 mL with ultrapure water. Before

**Table 2**

Instrumental parameters used to determine Cl by monitoring the CaCl and SrCl molecules using HR-CS GFMA.

	CaCl		SrCl	
Electronic transitions (range of wavelengths)	$\text{X}^2\Sigma \rightarrow \text{C}^2\Pi$ (364 – 402 nm) $\text{X}^2\Sigma \rightarrow \text{A}^2\Pi$ (604 – 636 nm)		$\text{X}^2\Sigma^+ \rightarrow \text{B}^2\Sigma^+$ (646 – 689 nm)	
Wavelength of the central pixel (samples analyzed at each wavelength)	377.501 nm (SRM 1575, CRM 686-1, SRM 2692c, SRM 1549) 620.862 nm (NCS ZC 81002b, BCR 460, ERM EC681, SRM 1568b)		635.862 nm (SRM 1575, SRM 1568b, SRM 1549)	
Detector pixels summed per line (resolution)	3 (~2.20 pm for 377.501 nm; ~4.00 pm for 620.862 nm)		3 (~4.15 pm)	
Chemical modifiers	Ca (400 $\mu\text{g}$ ) Pd (as nitrate – 20 $\mu\text{g}$ )		Sr (100 $\mu\text{g}$ ) Zr (permanent – 400 $\mu\text{g}$ ) + Pd (as nitrate – 20 $\mu\text{g}$ )	
Sample mass range for samples directly analyzed as solids	SRM 2692c	0.25–0.60 mg	SRM 1575	0.15–0.30 mg
	BCR 460	0.25–0.60 mg	SRM 1568b	0.20–0.35 mg
	NCS ZC 81002b	0.20–0.50 mg		
	SRM 1575	0.50–0.70 mg		
	SRM 1568b	0.15–0.30 mg		
	ERM EC681	0.25–0.50 mg		
	CRM 686-1	0.30–0.50 mg		
Temperature program				
Stage	Temperature/ $^{\circ}\text{C}$	Ramp/ $^{\circ}\text{C s}^{-1}$	Hold/s	Ar gas flow/ $\text{L min}^{-1}$
Drying	90	30	20	2.0
Drying	$110^{\text{a}}/130^{\text{b}}$	30	20	2.0
Pyrolysis	$700^{\text{a}}/600^{\text{b}}$	50	10	2.0
Vaporization	$2200^{\text{a}}/2300^{\text{b}}$	3000	5	0
Cleaning	2600	100	4	2.0

<sup>a</sup> CaCl.

<sup>b</sup> SrCl.

analysis and to adjust Cl concentration to the linear range of the calibration curve, further dilution of this suspension with ultrapure water (1:50) was carried out. Instrumental parameters used for analysis of the samples are described in Table 2.

The accessory (SSA 600) used allows for automatic weighing and transport of the samples to the furnace by means of a pair of tweezers. For the CRMs analyzed as solids, after first taring the empty sample platform, an adequate mass of the solid sample was deposited in the graphite platform to be weighed. Afterwards, 10  $\mu\text{L}$  of the molecule forming and the chemical modifier solutions (prepared as described in Section 2.2) were directly pipetted over the samples. Finally, the loaded platforms were transported to the graphite furnace and were subjected to the corresponding temperature program in Table 2, which was carefully optimized for the CaCl molecule as described in Section 3.2. For SRM 1549 non-fat milk powder, 10  $\mu\text{L}$  of the suspension (homogenized in an ultrasonic bath for 1 min before analysis), plus 10  $\mu\text{L}$  of the modifier and 10  $\mu\text{L}$  of the molecule forming agent were placed on the empty platform and were also subjected to the corresponding temperature program in Table 2.

In the case of the analysis based on the formation of the SrCl molecule, the method described in the work by Pereira et al. [20] was used with little modifications. In particular, graphite platforms were treated with Zr as permanent chemical modifier before the procedure described above was executed. For this purpose, 40  $\mu\text{L}$  of a 1 g L<sup>-1</sup> Zr solution were loaded onto the platform and subsequent thermal treatment in the graphite furnace was carried out. This protocol was repeated 10 times.

In all cases, quantitation was performed by calibration with aqueous standards. To this end, calibration curves prepared with one blank and five Cl standards covering the interval 100–800 ng (CaCl line

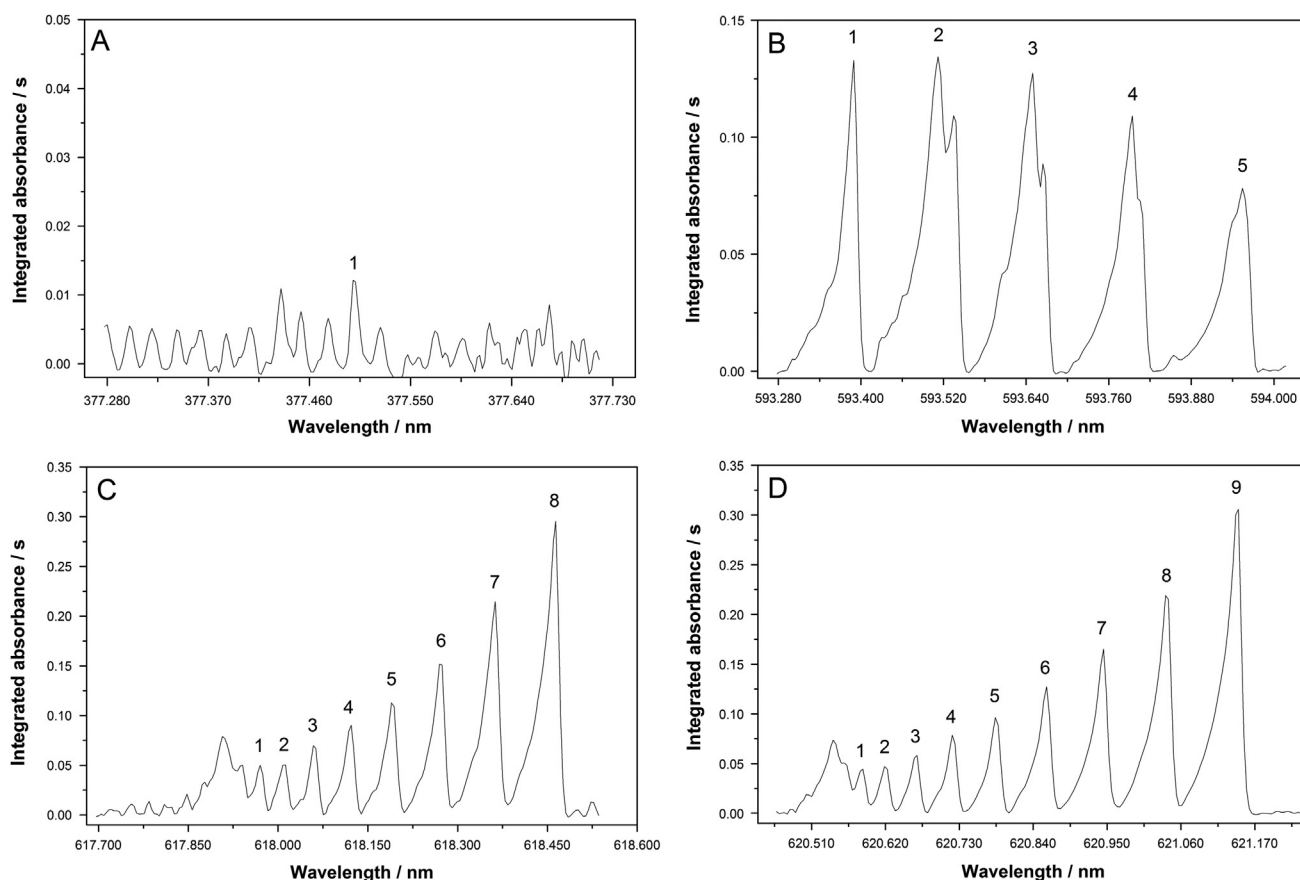
at 377.501 nm) and 20–100 ng (CaCl line at 620.862 nm and SrCl line at 635.860 nm) were used.

For every determination, five replicates of each CRM were analyzed and the median of the five results was taken as representative value [24]. In all cases, integrated absorbance ( $A_{\text{int}}$ ) was selected as measurement mode and the sum of the signals obtained for 3 pixels (the central pixel of each line plus the two adjacent ones,  $\text{CP} \pm 1$ ) was considered as the analytical result for each line studied.

### 3. Results and discussion

#### 3.1. CaCl molecular absorption spectra

As described in the classical literature [25], the CaCl molecule presents a series of absorption bands in the visible and ultraviolet regions of the electromagnetic spectrum. Typical absorption profiles acquired with HR-CS GFMA for the four more intense bands described for this molecule are depicted in Fig. 1. These spectra were obtained after vaporization of a Cl solution (100 ng Cl) under the conditions listed in Table 2, but centring the spectral window at wavelengths permitting to obtain the broadest overview of the molecular transitions in each case. As seen in Fig. 1, all systems present a structure of fine rotational lines, all of them corresponding to the  $\Delta v=0$  vibrational band of the corresponding electronic transitions:  $X^2\Sigma \rightarrow C^2\Pi$  for the band in the ultraviolet region (A,  $\lambda_{\text{max}}=377.501$  nm),  $X^2\Sigma \rightarrow B^2\Sigma$  for the band in the orange region (B,  $\lambda_{\text{max}}=593.390$  nm) and  $X^2\Sigma \rightarrow A^2\Pi$  for the two bands in the red region (C,  $\lambda_{\text{max}}=618.464$  nm and D,  $\lambda_{\text{max}}=621.146$  nm). This well resolved fine structure simplifies the procedure for setting the baseline as compared to other molecules giving rise to very broad bands [26], as is the case of AlCl [22]. On the



**Fig. 1.** Wavelength resolved time-integrated molecular absorption spectra for the four more intense systems of CaCl corresponding to the  $\Delta v=0$  vibrational band of the following electronic transitions: A)  $X^2\Sigma \rightarrow C^2\Pi$  ( $\lambda_{\text{max}}=377.501$  nm); B)  $X^2\Sigma \rightarrow B^2\Sigma$  ( $\lambda_{\text{max}}=593.390$  nm); C)  $X^2\Sigma \rightarrow A^2\Pi$  ( $\lambda_{\text{max}}=618.464$  nm) and D)  $X^2\Sigma \rightarrow A^2\Pi$  ( $\lambda_{\text{max}}=621.146$  nm). All spectra were obtained by vaporization of 100 ng Cl (as NaCl solution), 20  $\mu\text{g}$  Pd (as nitrate) and 400  $\mu\text{g}$  Ca, and applying the temperature program described in Table 2.



other hand, the existence of these different systems showing different sensitivities can be particularly useful in the case of direct solid sample analysis, as it opens the possibility to analyze samples with different Cl contents. These aspects will be studied in detail in Section 3.3.

### 3.2. Optimization of the working conditions for Cl determination after formation of the CaCl molecule in HR-CS GFMA: chemical modifiers and temperature program

In order to select the best working conditions for the formation of the CaCl molecule and for the measurement of its molecular absorption with HR-CS GFMA, all optimization experiments were carried out with aqueous solutions of Cl and monitoring the CaCl absorption at 620.860 nm, one of the most sensitive lines for this molecule, unless otherwise stated.

The first parameter to be optimized was the mass of Ca added to the graphite furnace. Ca, as the molecule-forming agent, needs to be in great excess in the furnace in order to ensure complete reaction with the analyte, thus assuring that variations in the analytical signal solely respond to variations in the amount of analyte (and not in the amount of Ca) present in the sample. For this optimization, 40 ng Cl were vaporized with increasing mass of Ca added to the furnace, in the presence of Pd(NO<sub>3</sub>)<sub>2</sub> as chemical modifier and applying the temperature program shown in Table 2. As shown in Fig. 2A where the evolution of the analytical response towards higher Ca mass is depicted, a fairly constant response is obtained for Ca mass higher than 400 µg. Before selecting this mass of Ca for further experiments, and taking into account that development of a method for direct solid sample analysis was intended, the optimization was also carried out monitoring the line at 377.501 nm (of much lower sensitivity, see Section 3.3), and vaporizing 400 ng Cl, to verify that the same behavior was observed for significantly higher Cl amounts. Similar results were also obtained in this case, and 400 µg Ca was finally selected as the optimum value for all further experiments.

At a second stage, selection of a chemical modifier was investigated. In fact, and as reported in all works considering Cl determination by means of HR-CS GFMA, addition of a proper chemical modifier seems mandatory for increasing the stability of the different chlorine molecules tested during the pyrolysis and vaporization stages. For this purpose, the use of both permanent modifiers, such as Zr [20], and non-permanent modifiers, such as Sr [17] or a mixture of Ag and Sr [18], were proposed in the literature.

Generally speaking, and with the exception of analytes prone to strongly interact with graphite, similar effects can be often obtained for MAS with permanent and non-permanent modifiers and a great deal of examples of both types of strategies can be found in the literature [11]. In spite of this fact, some authors prefer the use of permanent modifiers as a means to simplify the analytical procedure. In this particular case, and considering that the molecule forming agent solution has to be added to the sample before analysis anyway, the addition of a second solution with the modifier was not considered a serious complication to the experimental protocol, and only the use of non-permanent modifiers was considered. Taking also into account our positive experience with platinum group metals modifiers for MAS, addition of Pd, either as nitrate or as nanoparticles, and addition of Pt as nanoparticles was investigated in further experiments.

While addition of all three modifiers provided similar well-defined peaks and similar thermal stabilization for the CaCl molecule (see below for details), Pd nitrate was finally selected as the best option. The Pt nanoparticles provided slightly lower sensitivity for the CaCl molecule than Pd modifiers, and yielded elevated blank values probably due to some Cl contamination in the reagents used to synthesize these nanoparticles [23].

The mass of Pd(NO<sub>3</sub>)<sub>2</sub> added was subsequently optimized (see Fig. 2B). This figure shows the integrated absorbance recorded for 40 ng Cl with increasing mass of Pd (as nitrate), in the presence of

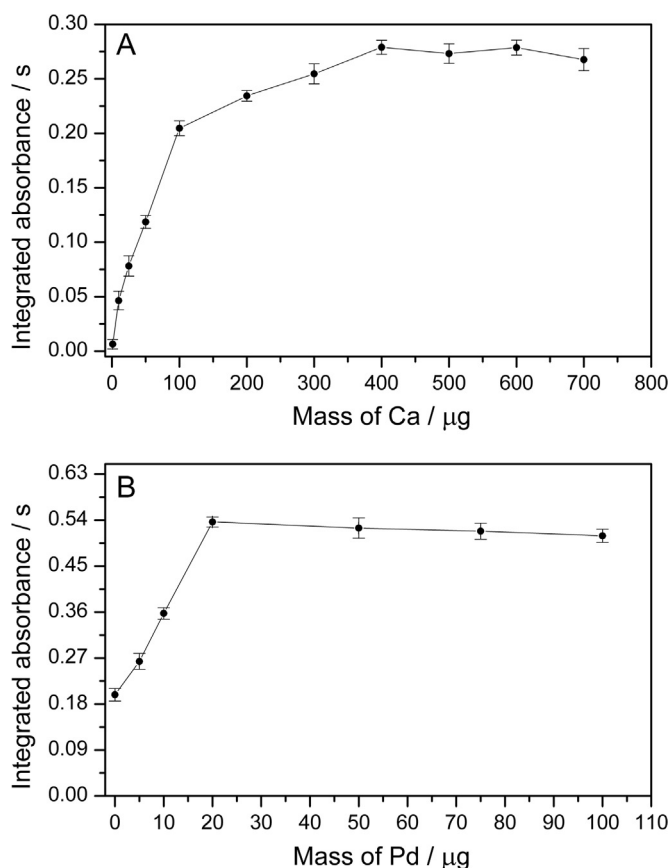


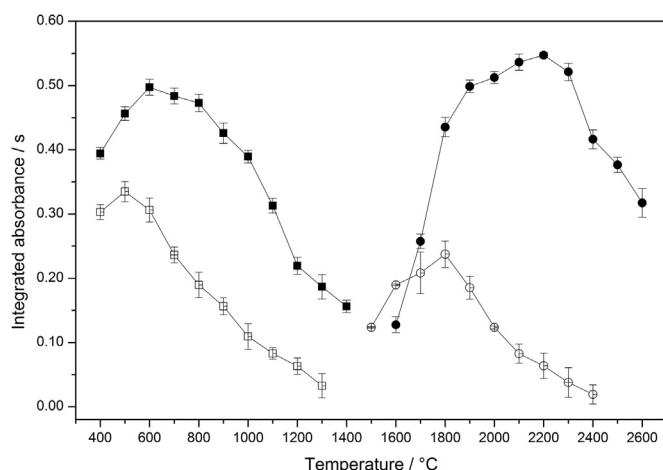
Fig. 2. (A) Optimization of the amount Ca added. This curve was obtained upon vaporization of 40 ng Cl (as NaCl solution), with the addition of 20 µg of palladium (as nitrate) by monitoring the 620.862 nm CaCl molecular absorption line. (B) Optimization of the amount of Pd added. This curve was obtained in the same conditions described in A), but fixing the amount of Ca added to 400 µg, while varying the amount of Pd added. In both cases, uncertainties are expressed as the standard deviation of three replicates.

400 µg Ca and applying the temperature program shown in Table 2. As seen from this figure, best results were obtained when masses of Pd higher than 20 µg were added to the platform. The study was also repeated using significantly higher mass of Cl (400 ng Cl measured at 377.501 nm). Similar results were obtained in this case, and 20 µg Pd were finally selected for further experiments.

Fig. 3 shows the pyrolysis and vaporization curves obtained for 40 ng Cl+400 µg Ca, both with and without the addition of Pd as chemical modifier. As seen from this figure, the benefits of Pd as chemical modifier are twofold. First, it significantly improves sensitivity for the CaCl molecular absorption at all temperatures tested. Second, it ensures stability until 900 °C for the pyrolysis stage. As for the vaporization, maximum absorption signals are obtained for 2000–2200 °C and 1800 °C, respectively, both in the presence and in the absence of Pd.

Considering that no significant differences were observed for the temporal profile of the signals at any of the different temperatures providing the maximum integrated absorbance results, a vaporization temperature of 2200 °C was finally chosen for further work. The pyrolysis temperature was fixed at 700 °C, which permitted decomposition of the matrices of all samples studied. Only in the case of the two carbon samples and the iron oxide sample some residues were left on the platform after analysis. Removal of these residues with a brush after every determination was sufficient for obtaining good results also for these samples.

The use of this mild temperature program has a positive effect on the lifetime of all graphite parts, which is usually compromised for molecular absorption methods needing a high concentration for the



**Fig. 3.** Pyrolysis (squares) and vaporization (circles) curves obtained for 40 ng of Cl (as NaCl solution) +400 µg Ca both with the addition of 20 µg Pd (filled symbols) and without any chemical modifier (empty symbols), when monitoring the 620.862 nm CaCl molecular absorption line. The vaporization ( $T_{\text{vap}}$ ) and pyrolysis ( $T_{\text{pyr}}$ ) temperatures selected for establishing the pyrolysis and vaporization curves, respectively, were  $T_{\text{vap}}=2200$  °C and  $T_{\text{pyr}}=700$  °C. Uncertainties are expressed as the standard deviation of three replicates.

molecule forming agent. In particular, each graphite tube and platform could be used for about 200–250 heating cycles.

### 3.3. Selection of lines and analytical properties of the method

When aiming at the direct analysis of solid samples, the availability of different absorption lines for a given analyte is always desirable to enable direct analysis of solid samples with different analyte contents [27,28]. In this sense, the monitoring of the rotational structure of a molecular absorption band usually offers interesting characteristics as, very often, several analytically useful lines with different sensitivities lie in the narrow spectral window that can be recorded by HR-CS instruments. This opens the possibility to improve the LOD by combining several peaks of similar sensitivity, or enlarging the linear working range by selecting a less sensitive line, with the advantage that all this can be done *a posteriori*, without the need for repeating the measurement.

Both strategies were explored in this case for the four CaCl systems monitored. As shown in Fig. 1, three of the four bands monitored for the CaCl molecule show a sequence of absorption lines with different sensitivities, while the other band only shows one line potentially useful of much lower sensitivity. In this figure, each band has been identified with a letter (A, B, C, D) and all lines potentially useful have been identified with a number. For all of these lines (or their combinations), characteristic mass, linear range and LOD were studied and results are summarized in Table 3.

As seen from this table the most sensitive system (D,  $\lambda_{\text{max}}=621.146$  nm) provides the best LODs, of about 2–3 ng, for the most sensitive lines. These LODs can be further improved by combining the signal for several of the most sensitive peaks. For instance, it is possible to improve the LOD by a factor of 3 when combining the signal of the three most sensitive peaks for this system (peaks 7, 8 and 9 in Fig. 1; 0.75 ng Cl), in comparison to the LOD obtained when monitoring the most sensitive CaCl line only (621.146 nm, 2.7 ng Cl). This value is similar to those reported by Fechetia et al. (1.2 ng Cl) [18] or Pereira et al. (1.0 ng [20] and 0.85 ng Cl [21]) using the AlCl and SrCl molecules, respectively.

Contrary to what could be expected, selection of less sensitive lines did not result in an extension of the linear range and all peaks for a given band provided exactly the same upper limit: 200 ng Cl for band B ( $\lambda_{\text{max}}=593.390$  nm) and 300 ng Cl for bands C and D (

**Table 3**

Characteristic mass ( $m_0$ ), linear range and limit of detection for the CaCl rotational lines monitored under the conditions listed in Table 2. LODs were calculated as three times the standard deviation of the blank ( $n=10$ ) divided by the slope of the calibration curve, obtained as described in Section 2.3. Characteristic masses were calculated as 0.0044 divided by the slope of the calibration curve. Range of wavelength (A, B, C, D) and peak numbers between brackets refer to those used in Fig. 1.

Range of wavelength	Wavelength/nm (peak)	$m_0$ /ng	Linear range /ng	LOD /ng
A	377.501 (1)	25.9	up to 860	14.2
	593.390 (1)	0.759	up to 200	4.9
	593.512 (2)	1.02	up to 200	4.8
	593.650 (3)	0.846	up to 200	5.5
	593.795 (4)	1.26	up to 200	6.5
	593.954 (5)	1.76	up to 200	7.8
C	617.970 (1)	2.59	up to 300	14.2
	618.012 (2)	2.44	up to 300	7.0
	618.059 (3)	1.63	up to 300	4.9
	618.122 (4)	1.19	up to 300	5.7
	618.190 (5)	1.05	up to 300	8.7
	618.274 (6)	0.772	up to 300	5.8
	618.363 (7)	0.595	up to 300	4.7
	618.464 (8)	0.436	up to 300	5.3
D	620.587 (1)	3.38	up to 300	11
	620.623 (2)	2.32	up to 300	7.2
	620.667 (3)	1.76	up to 300	2.5
	620.719 (4)	1.33	up to 300	6.7
	620.788 (5)	1.07	up to 300	2.2
	620.862 (6)	0.800	up to 300	2.6
	620.945 (7)	0.677	up to 300	3.9
	621.041 (8)	0.524	up to 300	3.2
	621.146 (9)	0.400	up to 300	2.7
	(7)+(8)+(9)	0.072	up to 300	0.75

$\lambda_{\text{max}}=618.464$  nm and 621.146 nm, respectively). The band in the ultraviolet region (A,  $\lambda_{\text{max}}=377.501$  nm), is the only one that permitted expansion of the linear range to 860 ng. This seems to indicate that the reason for the loss of linearity is chemical (loss of efficiency for the formation of the CaCl molecule for high Cl concentrations) more than spectroscopic.

### 3.4. Direct analysis of solid samples

To validate the method developed, direct solid sample analysis of seven of the certified reference materials listed in Table 1 was carried out. Only SRM 1549 Non-fat milk powder was analyzed as an aqueous suspension due to its high Cl content. Selection of the lines used for analysis was made according to the expected Cl content for each sample. Therefore, the most sensitive band (D,  $\lambda_{\text{max}}=621.146$  nm) was used for analysis of four of the samples, including those with lower Cl contents. For convenience and considering that most lines for this band provided similar LODs, the line at 620.862 nm (peak 6 in Fig. 1), located in the centre of the spectrum, was used for the determinations. For the rest of the samples the less sensitive line at 377.501 nm was used. On the other hand, sample masses were adapted for each sample (see Table 2) in order to obtain signal intensities within the linear range of each absorption line. In any case, different sample masses within the typical HR-CS GFMS range for direct analysis (0.1–10 mg) could be used for other samples with different Cl contents.

As an example, Fig. 4 shows a three-dimensional spectrum of the CaCl band absorption in the vicinity of 620.862 nm for the vaporization of 0.513 mg of the polyethylene sample (ERM EC 681). The signal for the solid sample is unimodal and well-defined, which was always the case for all samples. Signals for the aqueous standards were very similar to that shown in Fig. 4, but only for Cl contents below 150 ng. Above this quantity, peaks started to show some tailing and even double peaks appeared. In any case, and despite these dissimilar signal

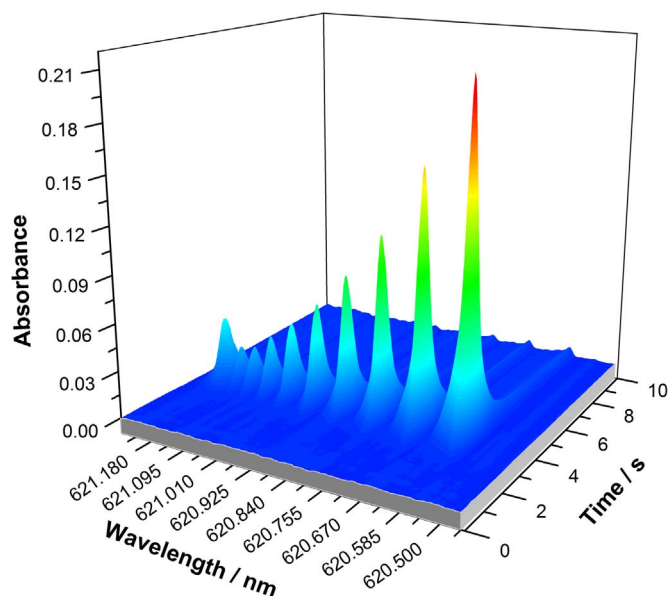


Fig. 4. Time and wavelength resolved absorbance spectrum for the CaCl molecule obtained after direct vaporization of 0.513 mg of a polyethylene sample (ERM EC 681), with the addition of 20  $\mu\text{g}$  of Pd and 400  $\mu\text{g}$  of Ca and under the working conditions gathered in Table 2.  $A_{\text{int}}=0.5829$  for the central peak at 620.862 nm.

Table 4

Determination of Cl in certified reference materials of various nature by means of solid sample analysis using HR-CS GFMS<sup>a</sup> (n=5) using the molecular absorption for CaCl and SrCl and the conditions described in Table 2. Uncertainties are expressed as 95% confidence intervals.

Certified reference material	Chlorine content/ $\mu\text{g g}^{-1}$		
	Certified value	CaCl molecular absorption	SrCl molecular absorption
NCS ZC 81002b	48.2 <sup>b</sup>	46 $\pm$ 5	NA <sup>c</sup>
CRM BCR 460	59 $\pm$ 18	42 $\pm$ 2	NA <sup>c</sup>
ERM EC681	92.9 $\pm$ 2.8	100.5 $\pm$ 9.7	NA <sup>c</sup>
SRM 1575	293 $\pm$ 20	291 $\pm$ 20	244 $\pm$ 56
SRM 1568b	301.1 $\pm$ 3.8	294 $\pm$ 33	306 $\pm$ 44
CRM 686-1	950 $\pm$ 60	1075 $\pm$ 120	NA <sup>c</sup>
SRM 2692c	1338 $\pm$ 22	1333 $\pm$ 100	NA <sup>c</sup>
NIST SRM 1549	10900 $\pm$ 200	10400 $\pm$ 650	8920 $\pm$ 630

<sup>a</sup> NIST SRM 1549 was analyzed as an aqueous dispersion.

<sup>b</sup> Informative value.

<sup>c</sup> Not analyzed.

profiles, integrated peak areas for the solid samples and the aqueous standards were always comparable so that quantitation remained possible.

The results obtained for Cl determination in the eight CRM are shown in Table 4. All results are in good agreement with certified values. On the other hand, precision can be considered as adequate for solid sample analysis, with values between 5% and 9% RSD for all CRM.

Analysis based on the measurement of the molecular absorption for the SrCl molecule using the method proposed by Pereira et al. [20] was also carried out, as a means of testing if the presence of Ca in the samples could pose potential problems for analysis after formation of the SrCl molecule. Three of the eight samples considered in this work were analyzed with this method, representing different analytical situations: one sample with a Ca/Cl ratio slightly lower than unity (SRM 1568b Rice flour), one sample with a Ca/Cl ratio close to unity (SRM 1549 Non-fat milk powder), and one sample with a Ca/Cl ratio well above unity (SRM 1575 Pine needles). Results for these analyses

are also shown in Table 4.

As seen from this table, the Ca/Cl ratio present in the CRM seems to exert a clear influence on the results obtained for Cl determination using the method based on the formation of the SrCl molecule. Results for the sample with lower Ca/Cl ratio (SRM 1568b; Ca/Cl ratio=0.4) are similar for the two methods, either based in the CaCl molecule or in the SrCl molecule. In both cases a good agreement with the certified value is obtained based on a Student's *t*-test at a confidence level of 95%, and similar precision values are also obtained based on an F-test at the same confidence level ( $F_{\text{cal}}=1.73$ ;  $F_{\text{crit}}=6.388$ ).

The situation changes when the Ca/Cl ratio increases. For SRM 1549 (Ca/Cl ratio=1.2) and SRM 1575 (Ca/Cl ratio=14), the method based on formation of the SrCl molecule provides values biased low, to the point that the result for the first sample is not in agreement with the certified value at the 95% confidence level. The result obtained for the second sample is still in agreement with the certified value at this confidence level, but precision for this method is significantly worse than precision obtained with the CaCl molecule based on an F-test at a confidence level of 95% ( $F_{\text{cal}}=7.91$ ;  $F_{\text{crit}}=6.388$ ). These results seem to support the idea indicated by our research group in a recent paper [22] that problems can be expected for determination of Cl by means of HR-CS GFMS with molecules such as AlCl (or SrCl), if elevated Ca contents are present in the samples to be analyzed and simple calibration with aqueous standards is intended to be used. The method proposed in this paper, based on the formation of the CaCl molecule does not show this limitation, providing good results for a wide variety of samples, while still offering a limit of detection below the ng level. This means that this method can compete in terms of LOD with more complex ones, such as those based on solid sample analysis electro-thermal vaporization-inductively coupled plasma mass spectrometry [29].

It is interesting to notice that, despite not being considered as the molecule forming agent in the first articles in which HR-CS GFMS was used [17], Ca has already been shown to be the preferred element for Br determination [11,30], a very good alternative for F determination [31] and, as shown in this work, a good choice for Cl determination via HR-CS GF MAS as well.

#### 4. Conclusion

This work adds a new molecule (CaCl) to the existing repertoire of molecules used for Cl determination by HR-CS GFMS, in order to extend the applicability of this technique to a wider range of analytical situations. Moreover, and in contrast to methods based in the formation of other molecules, the method developed permitted to obtain good results for samples naturally containing elevated Ca levels. This aspect is not trivial as Ca is an element commonly present at high concentrations in many samples where Cl determination needs to be performed, and having a robust methodology that can be deployed in such situations is clearly beneficial.

#### Acknowledgements

The authors acknowledge the funding from CTQ2015-64684-P (MINECO/FEDER) and from the Aragón Government (Fondo Social Europeo and project Innova-A1-020-15), as well as to Inycom S.A. A.G. thanks the Coordination for the Improvement of Higher Level Personnel (CAPES) for the doctoral and 'sandwich' scholarship (BEX 6349/15-3). P.C.N. also thanks the National Counsel of Technological and Scientific Development (CNPq).

#### References

- [1] J. Fauvarque, The chlorine industry, *Pure Appl. Chem.* 68 (1996) 1713–1720.
- [2] D. Lide, *CRC Handbook of Chemistry and Physics*, 90th ed., CRC Press, Boca Raton, USA, 2009.

- [3] P.A. Mello, J.S. Barin, F.A. Duarte, C.A. Bizzi, L.O. Diehl, E.I. Muller, E.M.M. Flores, Analytical methods for the determination of halogens in bioanalytical sciences: a review, *Anal. Bioanal. Chem.* 405 (2013) 7615–7642.
- [4] S.R. Krzyzaniak, R.F. Santos, F.M. Dalla Nora, S.M. Cruz, E.M.M. Flores, P.A. Mello, Determination of halogens and sulfur in high-purity polyimide by IC after digestion by MIC, *Talanta* 158 (2016) 193–197.
- [5] I. López-García, M. Sánchez-Merlos, M. Hernández-Córdoba, Slurry sampling device for use in electrothermal atomic absorption spectrometry, *J. Anal. At. Spectrom.* 12 (1997) 777–779.
- [6] M.G.R. Vale, N. Oleszczuk, W.N.L. dos Santos, Current Status of direct solid sampling for electrothermal atomic absorption spectrometry—A critical review of the development between 1995 and 2005, *Appl. Spectrosc. Rev.* 41 (2006) 377–400.
- [7] M. Resano, M. Aramendia, M.A. Belarra, High-resolution continuum source graphite furnace atomic absorption spectrometry for direct analysis of solid samples and complex materials: a tutorial review, *J. Anal. At. Spectrom.* 29 (2014) 2229–2250.
- [8] B. Welz, H. Becker-Ross, S. Florek, U. Heitmann, High-Resolution Continuum Source AAS: The Better Way to do Atomic Absorption Spectrometry, Wiley-VCH, Weinheim, Germany, 2005.
- [9] B. Welz, F.G. Lepri, R.G.O. Araujo, S.L.C. Ferreira, M.D. Huang, M. Okrus, H. Becker-Ross, Determination of phosphorus, sulfur and the halogens using high-temperature molecular absorption spectrometry in flames and furnaces—A review, *Anal. Chim. Acta* 647 (2009) 137–148.
- [10] D.J. Butcher, Molecular absorption spectrometry in flames and furnaces: a review, *Anal. Chim. Acta* 804 (2013) 1–15.
- [11] M. Resano, M.R. Flórez, E. Garcia-Ruiz, Progress in the determination of metalloids and non-metals by means of high-resolution continuum source atomic or molecular absorption spectrometry. A critical review, *Anal. Bioanal. Chem.* 406 (2014) 2239–2259.
- [12] K.I. Tsunoda, H. Haraguchi, K. Fuwa, Studies on the occurrence of atoms and molecules of aluminum, gallium, indium and their monohalides in an electrothermal carbon furnace, *Spectrochim. Acta Part B* 35 (1980) 715–729.
- [13] K.I. Tsunoda, K. Fujiwara, K. Fuwa, Determination of chlorine and bromine by molecular absorption of aluminum mono-halides at high-temperature, *Anal. Chem.* 50 (1978) 861–865.
- [14] K. Dittrich, B. Vorberg, J. Funk, V. Beyer, Determination of some nonmetals by using diatomic molecular absorbance in a hot graphite furnace, *Spectrochim. Acta Part B* 39 (1984) 349–363.
- [15] K. Dittrich, P. Meister, Molecular absorption spectrometry with electrothermal volatilization in a graphite tube Part 6. Determination of traces of chloride by molecular absorption of AlCl, GaCl and InCl molecules, *Anal. Chim. Acta* 121 (1980) 205–217.
- [16] P. Parvinen, L.H.J. Lajunen, Determination of chloride in drinking and ground water by AlCl molecular absorption spectrometry using graphite furnace atomic absorption spectrometer, *Talanta* 50 (1999) 67–71.
- [17] U. Heitmann, H. Becker-Ross, S. Florek, M.D. Huang, M. Okrus, Determination of non-metals via molecular absorption using high-resolution continuum source absorption spectrometry and graphite furnace atomization, *J. Anal. At. Spectrom.* 21 (2006) 1314–1320.
- [18] M. Fechetia, A.L. Tognon, M.A.M.S. da Veiga, Determination of chlorine in food samples via the AlCl molecule using high-resolution continuum source molecular absorption spectrometry in a graphite furnace, *Spectrochim. Acta Part B* 71–72 (2012) 98–101.
- [19] M.S.P. Enders, A.O. Gomes, R.F. Oliveira, R.C.L. Guimaraes, M.F. Mesko, E.M.M. Flores, E.I. Müller, Determination of chlorine in crude oil by high-resolution continuum source graphite furnace molecular absorption spectrometry using AlCl, InCl, and SrCl molecules, *Energy Fuels* 30 (2016) 3637–3643.
- [20] E.R. Pereira, B. Welz, A.H.D. Lopez, J.S. de Gois, G.F. Caramori, D.L.G. Borges, E. Carasek, J.B. de Andrade, Strontium mono-chloride — A new molecule for the determination of chlorine using high-resolution graphite furnace molecular absorption spectrometry and direct solid sample analysis, *Spectrochim. Acta Part B* 102 (2014) 1–6.
- [21] E.R. Pereira, L.M. Rocha, H.R. Cadorim, V.D. Silva, B. Welz, E. Carasek, J.B. de Andrade, Determination of chlorine in coal via the SrCl molecule using high-resolution graphite furnace molecular absorption spectrometry and direct solid sample analysis, *Spectrochim. Acta Part B* 114 (2015) 46–50.
- [22] F.V. Nakadi, M.A.M.S. da Veiga, M. Aramendia, E. Garcia-Ruiz, M. Resano, Chlorine isotope determination via the monitoring of the AlCl molecule by high-resolution continuum source graphite furnace molecular absorption spectrometry — a case study, *J. Anal. At. Spectrom.* 30 (2015) 1531–1540.
- [23] M. Resano, M.R. Flórez, Direct determination of sulfur in solid samples by means of high-resolution continuum source graphite furnace molecular absorption spectrometry using palladium nanoparticles as chemical modifier, *J. Anal. At. Spectrom.* 27 (2012) 401–412.
- [24] M.A. Belarra, M. Resano, J.R. Castillo, Theoretical evaluation of solid sampling-electrothermal atomic absorption spectrometry for screening purposes, *J. Anal. At. Spectrom.* 14 (1999) 547–552.
- [25] R.W.B. Pearse, A.G. Gaydon, The Identification of Molecular Spectra, 4th ed., Chapman and Hall, London, UK, 1976.
- [26] M. Aramendia, M.R. Flórez, M. Piette, F. Vanhaecke, M. Resano, Al determination in whole blood samples as AlF via high-resolution continuum source graphite furnace molecular absorption spectrometry: potential application to forensic diagnosis of drowning, *J. Anal. At. Spectrom.* 26 (2011) 1964–1973.
- [27] U. Heitmann, B. Welz, D.L.G. Borges, F.G. Lepri, Feasibility of peak volume, side pixel and multiple peak registration in high-resolution continuum source atomic absorption spectrometry, *Spectrochim. Acta Part B* 62 (2007) 1222–1230.
- [28] M. Resano, L. Rello, M. Flórez, M.A. Belarra, On the possibilities of high-resolution continuum source graphite furnace atomic absorption spectrometry for the simultaneous or sequential monitoring of multiple atomic lines, *Spectrochim. Acta Part B* 66 (2011) 321–328.
- [29] J.S. de Gois, E.R. Pereira, B. Welz, D.L.G. Borges, Application of direct solid sample analysis for the determination of chlorine in biological materials using electrothermal vaporization inductively coupled plasma mass spectrometry, *Spectrochim. Acta Part B* 105 (2015) 12–17.
- [30] M.R. Flórez, M. Resano, Direct determination of bromine in plastic materials by means of solid sampling high-resolution continuum source graphite furnace molecular absorption spectrometry, *Spectrochim. Acta Part B* 88 (2013) 32–39.
- [31] A.R. Borges, L.L. François, B. Welz, E. Carasek, M.G.R. Vale, Determination of fluorine in plant materials via calcium mono-fluoride using high-resolution graphite furnace molecular absorption spectrometry with direct solid sample introduction, *J. Anal. At. Spectrom.* 29 (2014) 1564–1569.