

# A closed system digestion and purification procedure for the accurate assay of chlorine in fossil fuels

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This paper describes a robust and quantitative method to separate, purify, and assay the amount of chlorine in fossil fuels using isotope dilution mass spectrometry. The digestion/extraction process uses Carius tubes containing the fossil fuel samples in the presence of HNO<sub>3</sub>, AgNO<sub>3</sub> and a <sup>37</sup>Cl spike. The closed system oxidation permits complete equilibration of the sample and spike Cl. The evolved chlorine is trapped as AgCl within the Carius tube, and can then be separated and cleaned. The purified AgCl is also amenable to isotopic analysis by solid or gas source isotope ratio mass spectrometry. For isotope dilution mass spectrometry, the chlorine can be readily measured in a thermal ionization mass spectrometer in a negative ion mode as <sup>37</sup>Cl/<sup>35</sup>Cl ratios with an approximate detection limit (LOD) of 0.3 µg Cl and a precision of 0.2%, relative. This technique may also be used to produce samples suitable for high precision measurements of chlorine isotopic variations in fossil fuels and chlorinated hydrocarbons.

## Introduction

Chlorine, sulfur, and mercury are environmentally significant contamination products of fossil fuel combustion. Robust methods have been developed at the National Institute of Standards and Technology (NIST) for the accurate assay of the latter two elements in Standard Reference Materials (SRMs);<sup>1,2</sup> however, a similar procedure is still needed for chlorine. As the power generation industry in the United States continues to grow, the need for fossil fuel SRMs accurately characterized for sulfur, mercury and chlorine content will increase as the Environmental Protection Agency (EPA) imposes stricter limits on power plant emissions for these elements. A recent economic impact study on the effect of accurately certified sulfur values in fossil fuel SRMs on the US economy<sup>3</sup> estimated a cost/benefit ratio of 113% and a net present value of more than \$400 million dollars. As new regulations pertaining to mercury and chlorine emissions are enforced, the importance of accurately assayed and readily available SRMs with these analytes will almost certainly reflect the sulfur experience.

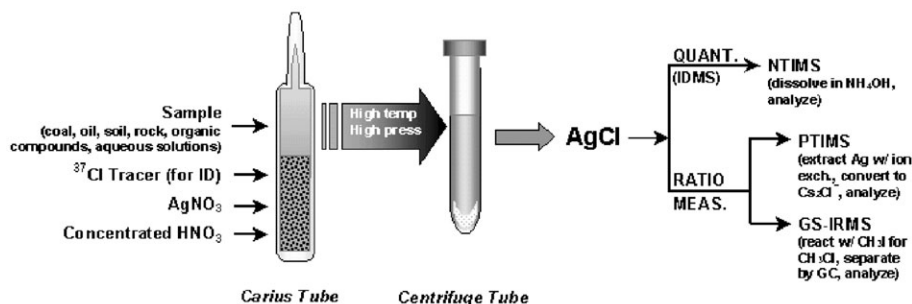
Chlorine acts both as a direct pollutant and as a catalyst in chemical reactions occurring within power plant exhausts. Most of the chlorine present in coal is emitted during combustion and there is evidence of soil, air, and water contamination from chlorine<sup>4</sup> in the regions surrounding larger thermoelectric power stations. During incineration, chlorine is also thought to play a significant role in the production and release of reactive gas mercury (RGM) to the atmosphere.<sup>5</sup> Moreover, the presence of chlorine in combustion gases increases plant operation costs by accelerating the degradation of the stainless steel components of the exhaust and heat transfer systems.<sup>6–8</sup> The increased utilization of the extensive and relatively untapped coal reserves in the deep, high-chlorine coal seams of the Illinois Basin have sparked concern over the potential impact of higher chlorine levels on both the environment and industry. Thus, accurate Cl assays of the feed material for power

generation are necessary in order to characterize and minimize deleterious effects from both perspectives.

A recent study by the Electric Power Research Institute (EPRI)<sup>9</sup> reported that while there are no commonly employed methods for the reliable measurement of chlorine in coal below 200 parts per million (ppm), there is a clear need for methods that can measure chlorine down to 100 ppm. A subsequent EPRI report<sup>10</sup> identified a routine method that could potentially achieve reproducible results down to 10 ppm chlorine in coal; however, accurate standards are needed to calibrate and verify such results, especially at the lower concentration range for chlorine.

Common chlorine extraction/separation methods typically require several stages during the purification/extraction process, thereby making quantitation difficult. Recently, in an attempt to improve the accuracy and precision of chlorine measurements, isotope dilution mass spectrometry (IDMS) was coupled with pyrohydrolysis,<sup>11</sup> a frequently used chlorine extraction method for geological samples. While an improvement over existing extraction method, this approach required a quantitative recovery of the sample/spike mix to assure isotopic equilibration. This is sometimes difficult to achieve and impossible to ensure.

In an effort to overcome these difficulties, Carius tube combustion was adapted for the extraction and isolation of chlorine. This method has already proven to be extremely effective for the extraction of sulfur and mercury from coals and other fossil fuels.<sup>1,2,12–14</sup> By combining this technique with isotope dilution negative ion thermal ionization mass spectrometry (ID-NTIMS), accurate chlorine quantitation is readily achieved (Fig. 1). The high temperature, high-pressure and closed system nature of Carius combustion is well suited to light element extractions that might otherwise be compromised during digestion and consequent volatilization. In fact, Carius combustion has been used in organic microanalysis since the 1940s for the quantitative determination, by gravimetry, of halogens and sulfur in organic compounds and matrices.<sup>15–17</sup>



**Fig. 1** Schematic view of the analytical procedure. Abbreviations are: ID (isotope dilution), IDMS (isotope dilution mass spectrometry), NTIMS (negative ion thermal ionization mass spectrometry), PTIMS (positive ion thermal ionization mass spectrometry), GS-IRMS (gas source isotope ratio mass spectrometry), GC (gas chromatography).

Simplicity and selectivity are its distinctive traits; extraction and separation are coupled in a single step, while the environment within the Carius tube assures equilibration of spike and sample without concomitant loss of either component.

## Experimental

### Digestion and separation apparatus

Modified Carius tubes were fabricated from thick wall borosilicate tubing (Fig. 2). The centrifuge tubes were 15 ml graduated tubes made of LDPE with screw caps. The pipettes were standard Pasteur pipettes.

### Reagents

High purity water was prepared by sub-boiling distillation while the ammonia solution was prepared by bubbling high purity  $\text{NH}_3$  through a water scrubber and into quartz distilled water, chilled with ice. Commercial high purity Optima® grade  $\text{HNO}_3$  (Fisher Chemical, 1 Reagent Ln, Fairlawn, NJ 07410) as well as Ultrex®II ammonia from JT Baker (Mallinckrodt Baker, Inc., 222 Red School Ln, Phillipsburg, NJ 08865) were also used. A  $5000 \mu\text{g g}^{-1}$  Ag solution was prepared from high purity silver nitrate (99.9999%) from Aldrich (Sigma-Aldrich Corp., 3050 Spruce St, St. Louis, MO 63103). Chlorine spike was prepared as a  $775 \mu\text{g g}^{-1}$  enriched  $^{37}\text{Cl}$  solution by serial dilution of  $^{37}\text{Cl}$  enriched NaCl from Isotech, Inc. NIST SRM 919a (Sodium Chloride Clinical Standard) and SRM 975a (Absolute Isotopic Standard for Chlorine) were used for spike calibration. NIST SRM 1632c (Trace Elements in Coal) was used as a control, and SRMs 2692b, 2685b and 2682b (Sulfur and Mercury in Coal) were run as samples.

### Digestion of spiked samples and controls

Samples were weighed out (typically 0.25–0.3 g) in glass boat funnels and transferred to the pre-cleaned and dried Carius tubes. Cleaning procedures are described in detail in the Cleaning/blank study section. Aliquots of the spike and  $\text{AgNO}_3$  solutions were added by weight to the Carius tubes using dropper bottles. The amount of  $^{37}\text{Cl}$  spike added to the sample was calculated to give a measured  $^{37}\text{Cl}/^{35}\text{Cl}$  ratio between 1 and 2, except for SRM 2682b which had a lower estimated concentration of Cl, and was spiked to give an estimated  $^{37}\text{Cl}/^{35}\text{Cl}$  ratio of 6. Excess  $\text{AgNO}_3$  (ca. 20% excess)

was then added together with approximately 6 ml of concentrated  $\text{HNO}_3$ . Blanks and control samples (SRM 919a/975a) were prepared using a similar procedure.

The Carius tubes were set vertically in dry ice to freeze the sample solutions, and sealed with a gas–oxygen torch. The tubes were then placed in steel shells along with about 50 g of solid  $\text{CO}_2$  to equalize the pressure built up in the glass tubes when heated. Several grams of  $\text{NaHCO}_3$  had been previously placed in the shell to neutralize any acid that may be lost from the tube due to a pinhole leak or explosion during combustion. The samples were heated to ca.  $250^\circ\text{C}$  overnight (ca. 16 h) in an oven. After cooling to room temperature, the Carius tubes were removed from the steel shells and placed behind an explosion shield. The tubes were then further cooled to  $\sim 0^\circ\text{C}$  and the necks heated with a torch to open a small vent hole, releasing the internal pressure. The tubes were scored below the shoulder and cracked open by application of heat from a torch. The tops of the tubes were removed and the contents transferred into centrifuge tubes using a high-purity water rinse (final volume, 11–12 ml).

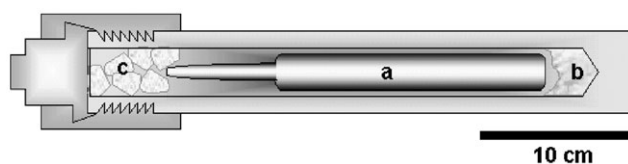
### Cleaning/blank study

The normal cleaning procedure for the Carius tubes was to first wash them with high purity (1:1)  $\text{HNO}_3$  by filling the tubes and heating to ca.  $70^\circ\text{C}$  for a couple of hours. The tubes were then rinsed and filled again with dilute high purity  $\text{HNO}_3$ , heated for a couple of hours, then allowed to stand overnight (ca. 16 h). The tubes were thoroughly rinsed and filled with high purity water, heated for a couple of hours, rinsed, refilled and allowed to stand overnight. The tubes were finally rinsed with high purity water and dried under a laminar flow hood. All of the cleaning took place in a class 10 clean room.

For the blank study, several tubes were also constructed with longer necks as part of a more aggressive cleaning study. In this study, the Carius tubes were filled with 6–7 ml of concentrated high purity  $\text{HNO}_3$  and sealed. They were then loaded into steel shells and heated to  $250^\circ\text{C}$  overnight, following the procedure for digestion of samples and controls. These tubes, after cooling, were opened, covered with Parafilm® and taken to a class 10 clean room. After rinsing with high purity water, each tube was filled with high purity water and allowed to stand for several hours. All tubes were dried under laminar flow in the clean room.

### Spike calibration standards

The spike calibration standards were made using NIST SRM 919a, a primary chlorine assay standard. The standard was serially diluted to a final concentration of ca.  $1000 \mu\text{g g}^{-1}$  Cl. This was done in triplicate so that any subsequent aliquoting or dilution errors could be readily identified. Approximately 0.25–0.3 g of each final solution was weighed into a centrifuge tube and mixed with 0.25–0.3 g of the  $^{37}\text{Cl}$  spike solution together



**Fig. 2** Carius tube inside its steel casing: (a) Carius tube; (b)  $\text{NaHCO}_3$ ; (c) “dry ice”.

with  $\sim 1$  g of a  $5000 \mu\text{g g}^{-1}$  high purity  $\text{AgNO}_3$  solution and about 5 ml conc.  $\text{HNO}_3$ . This was done in duplicate, and resulted in six calibrant solutions. The solutions were shaken vigorously and stored in the dark for about 2 h to assure equilibration. Each of the six calibration standards was run 1–3 times for a total of 11 runs. A standard solution of NIST SRM 975a, an isotopic standard for chlorine, was used to correct for instrumental mass fractionation as described in the mass spectrometry section.

### Separation of chlorine as AgCl

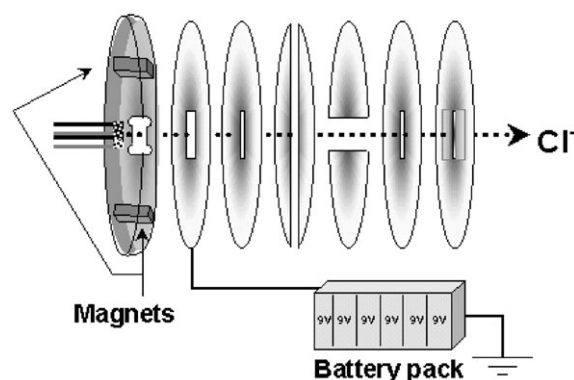
The centrifuge tubes, containing samples, controls and spike calibration standards, were placed in a centrifuge and spun down. The supernatant was removed using Pasteur pipettes, leaving the AgCl precipitate in the tubes. This precipitate was then rinsed and centrifuged twice more with dilute high-purity  $\text{HNO}_3$  before being dissolved in approximately 100  $\mu\text{l}$  of a 50% v/v high purity ammonia solution. The samples were capped and stored in a freezer prior to analysis. Care was taken at all stages to minimize the exposure of the AgCl solutions to light.

### Mass spectrometry

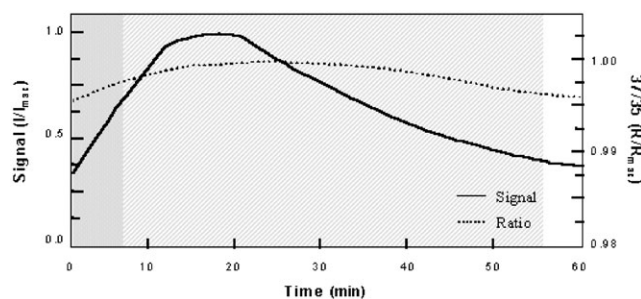
Measurements were made on an NIST designed 30 cm radius –  $90^\circ$  sector solid source, thermal ionization mass spectrometer equipped with a Faraday collector. Filament currents were controlled by a NIST designed dc power supply. Ionizing filament temperatures were read with an optical pyrometer.

A wide aperture thin lens source, modified for use with negative ions, was used for ion extraction, collimation and acceleration and is shown in Fig. 3. Pertinent modifications were as follows: (1) magnets were placed in the shield plate to deflect electrons produced at the filament, thereby preventing them from entering the lens stack where they could damage the slits; (2) six 9 V batteries, wired in series, were connected to the first lens plate to prevent the electrons from charging the lens and deflecting the ion beam.

The Re sample and ionization filaments were out-gassed at  $<10^{-4}$  Pa for 5 min at 2.5 A, then for 35 min at 3.5 A in a special filament out-gasser of NIST design. All filaments were also “flash cleaned” prior to use (to eliminate alkalis) by turning them on at 3.5 A for 5 s, then off for 5 s, over a period of 1 min (also at  $<10^{-4}$  Pa). Two side filaments were loaded under a laminar flow hood with *ca.* 9–12  $\mu\text{g}$  Cl (about 50% of mass per filament). The amount of solution needed to load a sample was typically 2–3  $\mu\text{l}$  for the spiked samples, 4–5  $\mu\text{l}$  for the unspiked samples and controls, and 9–10  $\mu\text{l}$  for the blanks. Samples were dried under a 250 W infrared heat lamp as they were loaded.



**Fig. 3** Modified wide aperture thin lens source. The Cl solutions were loaded on the side filaments of the filament assembly on the extreme left side of the figure. Ions were generated thermally and accelerated to and through the slit plate on the right side of the figure.



**Fig. 4** Typical variations observed in the Cl-signal and the measured Cl isotope ratio during the time of sample conditioning (darker shading) and data collection (lighter shading).

The loaded and dried filaments were then assembled in a triple filament configuration with a central Re ionizing filament and put into the mass spectrometer. The source chamber was then allowed to pump down to *ca.*  $10^{-4}$  Pa and, after filling the cold finger with liquid  $\text{N}_2$ , was opened to the flight tube and detector. The source vacuum was typically in the  $10^{-5}$  Pa range when the samples were being heated and ionized. Controlled heating was achieved by stepping the central filament current up by  $0.2 \text{ A min}^{-1}$  until a temperature of *ca.*  $1375^\circ\text{C}$  was reached ( $\sim 2.4 \text{ A}$ ), then the current was increased by  $0.1 \text{ A min}^{-1}$  to *ca.*  $1550^\circ\text{C}$  ( $\sim 3.0 \text{ A}$ ). The side filaments were then taken to approximately 0.5 A, and the center filament ramped a bit higher to  $1600\text{--}1610^\circ\text{C}$ . The beam was centered and focused to give maximum intensity and the baseline was measured. The mass ratio  $37/35$  ( $^{37}\text{Cl}/^{35}\text{Cl}$ ) was then measured in multiple blocks of 5 ratio sets over a period of 10–60 min. Data was generally taken over the period during which the Cl-signal reached its maximum intensity as shown in Fig. 4. The final Cl isotopic ratio precision for all sample runs was better than 0.3% (RSD).

Instrument mass fractionation was corrected using a T/E (true ratio/experimental ratio) correction. This was calculated by ratioing SRM 975a's certified  $37/35$  absolute abundance ratio to the average  $37/35$  ratio measured in the isotopic standard. This correction was computed and applied in a batch or bracketed mode to samples run between the standards used to monitor the instrument fractionation.

## Results and discussion

### Blank study

Typical blanks reported for chlorine analysis are procedure limited and are in the 1  $\mu\text{g}$  range. The use of high purity reagents and the reduction of sample handling during sample preparation often lead to a reduction of the blank. This study reports a total procedural blank of  $1.09 \pm 0.11 \mu\text{g Cl}$  ( $n = 6$ ) placing in a lower limit of detection ( $3\sigma$ ) at approximately  $0.33 \mu\text{g Cl}$ . A much lower reagent blank (not carried through combustion) of  $0.23 \mu\text{g Cl}$ , suggests that the combustion stage is contributing the bulk of the blank, *ca.*  $0.86 \mu\text{g Cl}$ . This is not surprising when one takes into account the high temperatures and pressures experienced during combustion and its effect on the walls of the Carius tube. These extreme conditions may induce leaching from the internal surfaces of the glass tube of substances that were not removed during normal cleaning procedures or were intrinsic to the glass itself.

By cleaning the Carius tubes under combustion conditions, it was hoped that leaching might be enhanced and that would be more effective in reducing the blank. Therefore, tubes were designed with longer necks that could be sealed and cleaned under combustion conditions, then opened and resealed as described in the preceding section on cleaning procedures. The results of this study, listed in Table 1, suggest that this more aggressive method of cleaning did not reduce the blank to a

**Table 1** Comparison of chlorine blanks using different cleaning procedures

	Cl/ $\mu\text{g}$	$\sigma/\mu\text{g}$
Reagent blank <sup>a</sup>	0.23	$\pm 0.08$
Procedure blank (A) <sup>b</sup>	1.10	$\pm 0.09$
Procedure blank (B) <sup>c</sup>	1.07	$\pm 0.18$

<sup>a</sup> Values based on three runs each of two independent samples. <sup>b</sup> Values based on two runs each of two independent samples. <sup>c</sup> Values based on two runs of one independent sample.

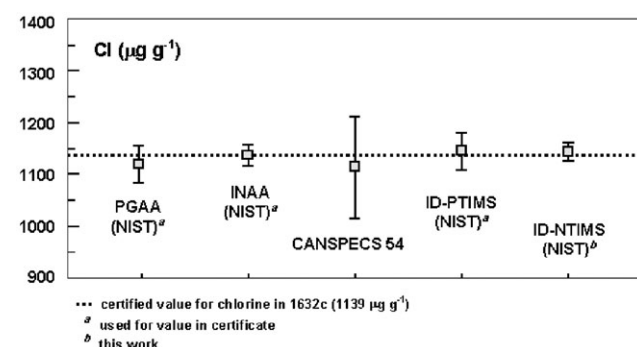
significant degree. This suggests that either there must be some other source for this portion of the blank or that the possible blank reservoir represented by the interior of the tube is effectively infinite. A leaching front progresses into the glass, leaving behind a porous glass interface that communicates the blank Cl with the reacting solvents. At present, the data do not allow for a distinction between these possible sources.

### Analysis of chlorine in coal

The accuracy of the Carius combustion ID-NTIMS method was validated by analysing NIST SRM 1632c, Trace Elements in Coal. The average value from the analysis of four independent samples of SRM 1632c (including replicates) was  $1140.05 \pm 6.25 \mu\text{g g}^{-1}$  Cl (1 sd). This value agrees with the certified value for Cl in SRM 1632c and with the value obtained by using pyrohydrolysis combined with ID-PTIMS,<sup>11</sup> as shown in Table 2. Although the precision cited for NTIMS appears to be better than PTIMS, the higher standard deviation observed for the PTIMS measurements is most likely a reflection of the variability in Cl recovery during pyrohydrolysis and thus does not reflect the intrinsic precision of the PTIMS method. This emphasises the dependence of the pyrohydrolysis technique on achieving quantitative recovery of all Cl, due to a lack of equilibration between the tracer and the sample during the extraction (pyrohydrolysis) stage. The measured value from the Carius ID-NTIMS technique also agrees well with individual measurements obtained by each of the individual techniques used for certification of SRM 1632c, neutron activation analysis (INAA) and prompt gamma activation analysis (PGAA), and with values from a CANSPECS

**Table 2** Comparison of results produced by isotope dilution positive ion mass spectrometry (ID-PTIMS) and isotope dilution negative ion mass spectrometry (ID-NTIMS)

	Cl/ $\mu\text{g g}^{-1}$	$\sigma/\mu\text{g g}^{-1}$	RSD (%)
Certificate	1139	$\pm 41$	3.6
ID-PTIMS	1143.9	$\pm 31.7$	2.77
ID-NTIMS	1140.0	$\pm 6.2$	0.55

**Fig. 5** Comparison of measured chlorine concentrations for NIST SRM 1632c, Trace Elements in Coal.**Table 3** Comparison of chlorine concentrations measured in CANSPECS round robins to those measured by ID-NTIMS

		Cl/ $\mu\text{g g}^{-1}$	$\sigma/\mu\text{g g}^{-1}$	RSD (%)
2692b	CANSPECS 2000–2	1593	$\pm 200$	12
	Carius/NTIMS <sup>a</sup>	1650	$\pm 24$	1.5
2685b	CANSPECS 58	530	$\pm 161$	30
	Carius/NTIMS <sup>a</sup>	540	$\pm 3$	0.6
2682b	CANSPECS 55	76	$\pm 102$	—
	Carius/NTIMS <sup>b</sup>	18.4	$\pm 0.6$	3.3

<sup>a</sup> Values based on two runs of single independent samples. <sup>b</sup> Values based on two runs each of two independent samples.

54 round robin analysis using ASTM D 4208, bomb combustion-ion selective electrode (Fig. 5).

The Carius ID-NTIMS method was also applied to three different SRM coals with varying chlorine contents: 2692b, a bituminous coal (*ca.*  $1600 \mu\text{g g}^{-1}$  Cl) with  $7.90 \pm 0.30\%$  ash content and  $1.24 \pm 0.03\%$  moisture content; 2685b, a bituminous coal (*ca.*  $530 \mu\text{g g}^{-1}$  Cl) with  $15.94 \pm 0.30\%$  ash content and  $2.32 \pm 0.06\%$  moisture content; 2682b, a subbituminous coal (*ca.*  $76 \mu\text{g g}^{-1}$  Cl) with  $6.32 \pm 0.42\%$  ash content and  $12.79 \pm 1.29\%$  moisture content. The results of these analyses are shown in Table 3. The values obtained agree closely with the estimated values for the coals with higher Cl concentrations, SRM 2685b and 2692b, based on consensus values from CANSPECS 58 and CANSPECS 2000–2, respectively. However, the concentration measured in the lower-level subbituminous coal,  $18.3 \pm 0.6 \mu\text{g g}^{-1}$  (1 sd) is significantly lower than the reported CANSPECS 55 consensus value of  $76 \mu\text{g g}^{-1}$ . However, taking into account the high standard deviation of the CANSPECS 55 number, the value falls well within the statistical uncertainty.

The method employed by the CANSPECS 55 round robin for chlorine analysis was ASTM D 4208, Bomb Combustion Ion-Selective Electrode. ASTM reports a method reproducibility of only  $77 \mu\text{g g}^{-1}$ . Additionally, this method was one of several evaluated in an EPRI study evaluating chlorine analysis methods. EPRI stated that of the three chlorine methods they compared: “ASTM D 2631 Bomb Combustion Potentiometric Titration, ASTM D 4208 – Bomb Combustion Ion Selective Electrode, and Bomb Combustion Ion Chromatography. None of these methods could measure chlorine in coal with acceptable accuracy or precision, particularly at levels below  $200 \mu\text{g g}^{-1}$  [equivalent to parts per million (ppm)].”<sup>9</sup>

### Additional applications

In addition to quantitative chlorine analysis, the Carius extraction procedure can be readily adapted for high precision Cl isotope ratio measurements as shown in Fig. 1. Chlorine isotopic ratios could be measured by either the highly precise positive ion thermal ionization mass spectrometry or by gas source isotope ratio mass spectrometry (GS-IRMS). Variations in chlorine isotopic ratios have proved useful in geologic/hydrologic applications, however recent studies have shown that variations in Cl isotopic ratios can be used as a tracer of specific chlorinated organic contaminants.<sup>18–21</sup> Closed system Carius tube digestion for Cl isotopic analysis should be quite useful in monitoring sources, migration and degradation of these harmful compounds.

### Conclusion

Chlorine, sulfur and mercury are the three most significant and therefore most carefully monitored pollution by-products of fossil fuel combustion. Definitive measurement techniques for accurate assays of these elements in fossil fuels are in place at NIST for sulfur and, more recently, for mercury. The value of

the accurate measurements for these elements on the fossil fuel SRMs and their consequent impact on the US economy have been well documented. It is expected that the development of an accurate assay technique for chlorine in the same fossil fuels may have a similar impact. In addition, the power industry has shown an interest in chlorine analysis, exploring techniques for quantifying chlorine in coal. Thus, there is a need to develop a high accuracy technique for chlorine certification in coals and other fossil fuels.

This paper demonstrates that Carius combustion combined with NTIMS can provide robust and accurate values for chlorine in coal. It does not suffer from the complications of other commonly used extraction methods. The closed system extraction allows little chance for loss and assures equilibration of the sample and spike making ID analysis possible. Additionally, since the sample and spike chlorine are trapped as AgCl after extraction, a simple dissolution in ammonia and separation from the ash components of the sample are all that is required for sample preparation. Final analysis by NTIMS is also an advantage, in that detection limits are not really an issue. The amount of sample loaded for analysis by NTIMS may be adjusted to gain adequate intensity for an accurate ratio measurement.

Finally, additional applications such as the measurement of chlorine isotopic ratios are of a more exploratory nature, and have yet to be tried using this method. However, if Carius combustion proves robust for high-precision chlorine isotope ratio measurements, it may provide a straightforward way of assessing CAH contamination sources and the evolution of these chlorinated contaminants at a particular site.

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