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Measurement of soil/dust arsenic by gas phase chemiluminescence

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ABSTRACT

A gas phase chemiluminescence (GPCL)-based method for trace measurement of arsenic has been recently described for the measurement of arsenic in water. The principle is based on the reduction of inorganic As to AsH_3 at a controlled pH (the choice of pH governs whether only As(III) or all inorganic As is converted) and the reaction of AsH_3 with O_3 to produce chemiluminescence (Idowu et al., Anal. Chem. 78 (2006) 7088–7097). The same general principle has also been used in postcolumn reaction detection of As, where As species are separated chromatographically, then converted into inorganic As by passing through a UV photochemical reactor followed by AsH_3 generation and CL reaction with ozone (Idowu and Dasgupta, Anal. Chem. 79 (2007) 9197–9204). In the present paper we describe the measurement of As in different soil and dust samples by serial extraction with water, citric acid, sulfuric acid and nitric acid. We also compare parallel measurements for total As by induction coupled plasma mass spectrometry (ICP–MS). As(V) was the only species found in our samples. Because of chloride interference of isobaric $ArCl^+$ ICP–MS analyses could only be carried out by standard addition; these results were highly correlated with direct GPCL and LC–GPCL results (r^2 = 0.9935 and 1.0000, respectively). The limit of detection (LOD) in the extracts was 0.36 μg/L by direct GPCL compared to 0.1 μg/L by ICP–MS. In sulfuric acid-based extracts, the LC–GPCL method provided LODs inferior to those previously observed for water-based standards and were 2.6, 1.3, 6.7, and 6.4 μg/L for As(III), As(V), dimethylarsinic acid (DMA) and monomethylarsonic acid (MMA), respectively.

1. Introduction

Arsenic (As) is the 20th most abundant element in the earth's crust. Some forms of As are extremely toxic; As is designated as a group A carcinogen for humans [1–3]. The USEPA has set a maximum contamination level (MCL) of As in drinking water of 10 μg/L [3]; similar limits exist through most of the world. Arsenic contamination in groundwater and thence drinking water has been and continues to be a major concern in eastern India and Bangladesh [4,5]. In many areas in the United States, groundwater contains more than 10 μg/L As [6,7]. Arsenic toxicity and health effects have been extensively discussed and it has been linked to many diseases and disorders [8–16]. Arsenic in water is usually inorganic, present as arsenite (As(III)) or arsenate (As(V)); organic forms such as methylarsenite, methylarsenate, dimethylarsenite and dimethylarsenate also occasionally exist in traces [17]. It has been suggested [18] that arsenic mutagenicity occurs because of the similarity of the chemistries of arsenic and phosphorus (P). The actual situation is likely to be much more complex. The simplistic mechanism above would not account for why As(III) is much more toxic compared to As(V) and P is exclusively present in biological systems in the +5 oxidation state. Moreover, As(V) toxicity appears to occur via its reduction by reduced glutathione to As(III) [12].

Electrochemical techniques are relatively affordable and highly sensitive. Various electrochemical measurement methods continue to be developed [19–24]; however, few are in practical use. We had developed one ourselves [25], only to discover that in real samples there are too many problems and calibration must be onerously frequent. Atomic spectrometry, typically combined with a front end separation technique, dominates present practice [17,26]. Paradoxically, countries which most need As measurement and speciation can least afford such techniques. At the other extreme, "Field Kits" are available for arsenic detection. These are based on reduction of As to AsH_3 that is then passed through a lead acetate-soaked filter to remove any generated H_2S, and then through a mercuric bromide impregnated filter. The latter turns yellow to brown depending on

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the level of As present. The ability of the kits to provide quantitative data at the regulation limit of 10 μg/L is questionable at best and aside from reliability there are other problems related to leakage of arsine from the generators, use of large sample volumes and chemicals, and thence generation of large volumes of waste, some of which includes lead and mercury [27,28]; others have pointed to the valuable information that the kits have nevertheless yielded [29].

Inspired by the original work of Fujiwara et al. [30] and Fraser et al. [31], in the last few years we developed a technique that provides a unique combination of sensitivity and affordability where sub-μg/L LODs can be reached with 2–3 mL samples on equipment costing <US$ 2500. In this technique, inorganic As can be speciated into As(III) and As(V) without chromatographic separation. Aqueous As is reduced by $NaBH_4$ to form AsH_3. This reduction is highly pH dependent—at low pH (<1) both As(III) and As(V) are reduced while at pH 4–7 only As(III) is reduced. The liberated arsine is reacted with ozone generated from ambient air in a reflective enclosure atop a photosensor module (PSM). All liquid handling is conducted by a fully automated syringe pump connected to a multi-port selector valve. Details appear in the original work [32]; As(III) can be determined at pH 4 and the solution can then be strongly acidified and As(V) then determined, or As(III) and total As can be separately determined at pH 4 and pH < 1, respectively, obtaining As(V) by difference. We will henceforth refer to this as the gas phase chemiluminescence (GPCL) method. The GPCL technique has equivalent sensitivity for As(III) and As(V) but does not respond well to organoarsenicals like dimethylarsinic acid (DMA) and monomethylarsonic acid (MMA). Arsenobetaine, which does not form a hydride, does not respond at all.

To speciate arsenic and use the same detection technique, the following strategy was developed [33]: (i) ion exchange chromatographic separation was first conducted using a bicarbonate/carbonate and carbonate/hydroxide eluent; (ii) the column effluent was segmented with nitrogen bubbles to minimize dispersion; (iii) the stream was flowed through a photoreactor (PR) that photodecomposed and oxidized all arsenic species into inorganic As(V); (iv) $NaBH_4$ and acid were added in separate streams continuously; (v) after ~12 s in a flow through reactor the gaseous AsH_3 and H_2/N_2 was separated in a gas liquid separator; and (vi) the AsH_3 entered the GPCL reactor where ozone was simultaneously introduced and the emitted light measured. In the following, this is referred to as the LC–PR–GPCL system.

In the context of ground water, arsenic content of soils is particularly important. In the present paper we establish a scheme of serial soil extraction with increasingly aggressive extractants and analyze these by GPCL as well as LC–PR–GPCL techniques and compare the results with those obtained by induction coupled plasma–mass spectrometry (ICP–MS), considered by many to be the benchmark measurement technique [34–37].

2. Experimental

2.1. Standards and reagents

Stock standards of 50 mg As/L were prepared. Inorganic As(III) and As(V) were prepared from As_2O_3 and $Na_2HAsO_4{\cdot}7H_2O$ (J. T. Baker), respectively. Solutions of As(III) were prepared in 0.3 M HCl and As(V) solutions were prepared in 1 mM HCl. MMA and DMA standard solutions were prepared from sodium monomethylarsonate sesquihydrate (97.3%, ChemService Inc.) and cacodylic acid (98%, Aldrich), respectively, in water. Lower concentrations were prepared by dilutions with (18.2 MΩ cm) Milli-Q deionized water (DIW). Other reagents used for arsine generation included 1 M sulfuric acid (EMD Chemicals Inc.) and 4% (w/v) $NaBH_4$ (98%, Aldrich) in 0.5 M NaOH (EMD Chemicals) and 1 mM Na_2EDTA (US Biochemicals). Chromatography used a step gradient from 4 mM Na_2CO_3–0.8 mM $NaHCO_3$ (Eluent A) to 60 mM Na_2CO_3–30 mM NaOH (Eluent B). To minimize As(III) oxidation in the chromatographic column under alkaline conditions, the DIW used for eluent preparation was degassed by ultrasonication under vacuum for 25 min prior to use. The ^{115}In isotope (95.7% natural abundance) from indium chloride (Strem Chemicals) was used as an internal standard for ICP–MS measurements; a stock solution of 1000 mg In/L was used.

2.2. Sample extraction

Two different strategies were used. One involved sequential extraction. This was performed by extracting ~0.5 g of the soil sample with 2 mL DIW in a 10 mL capacity centrifuge tube; the mixture was shaken for 1 min, ultrasonicated for 30 min and then centrifuged for 5 min at 2250 rpm. The supernatant was decanted off and labeled Extract 1A. The precipitate was re-suspended in a fresh 2 mL aliquot of DIW, and the process was repeated to obtain Extract 1B. This process was repeated with two sequential extractions with 10 mM citric acid (Fluka, Extracts 2A and 2B), 1 M H_2SO_4 (Extracts 3A and 3B) and 2 M HNO_3 (VWR, Extracts 4A and 4B). Blank extract solutions were analyzed in an identical manner to the sample extracts (including dilution—see below). Blank values were very small but were subtracted as applicable. At least three aliquots of each soil/dust sample were taken and the results reported are in terms of the mean and standard deviations of at least three analyses. The original <2 mL decantate was diluted to 10 mL in a volumetric flask prior to replicate analysis; occasionally, this was further diluted 2× prior to analysis.

Arsenic in six selected samples (~0.4–2 g each) was extracted with 7 mL 1 M H_2SO_4 (shake ~1 min, ultrasonicate 30 min, centrifuge 5 min and decant). A 5-mL aliquot of the supernatant was diluted by DIW to 25 mL. A 5-mL aliquot of this diluted extract was analyzed with and without spiking with a 1 μg/L As(III) standard to attain added levels of 0.0, 5.0, 10.0, and 15.0 μg/L added As in the final solution which was made up to 50 mL. The spiking and calibration standards were made in 20 mM H_2SO_4. The unspiked final diluted extract was analyzed in triplicate by GPCL. Another aliquot of this was brought to near-neutrality by addition of a calculated amount of NaOH and analyzed in triplicate by LC–PR–GPCL. For ICP–MS both unspiked and spiked extracts were analyzed to apply standard addition based quantitation; it was found early on that analysis of unspiked solutions alone do not lead to accurate quantitation. Due to matrix-induced signal suppression, the average recovery of a standard added to a typical sample extract was 85%.

2.3. Analysis methods

Initial screening experiments with LC speciation showed that none of our soil samples contained any As species other than As(V). The direct GPCL method was thus conducted in strong acid medium, which determines total As only. For the GPCL apparatus, see the detailed description in [32]. Briefly, to 3-mL sample delivered to the reactor, 1 mL of 2 M H_2SO_4 was added. Following a syringe wash, 0.5 mL of the $NaBH_4$ reagent is next added at a high speed (1.04 mL/s) to induce rapid mixing. After 60 s, the reactor exit valve is opened to allow the liberated arsine to proceed to the CL cell; the reactor solution is purged simultaneously with 25 cm^3/min of activated carbon filtered air. The PSM was operated at a control voltage of 0.85 V and a secondary amplifier gain of 1250×.

For a detailed description of the LC–PR–GPCL system, see Ref. [33]. For improved separation, in the present work different eluents (see Section 2.1) and chromatographic protocol were used. Each chromatographic cycle was 20 min; Eluent A was used for the first 6 min and switched to Eluent B for the next 8 min before being switched to Eluent A again. Chromatographic conditions are given in detail in Table S1 in supporting information (SI). The PSM was operated with a control voltage of 0.85 V and a secondary amplification of 1000×.

Quantification on an ICP–MS was performed on a single quadrupole instrument of 0.7 amu mass resolution (X-Series II ICP–MS, equipped with a Peltier-cooled nebulizer, Thermo Fisher Scientific). Instrument operating condition and mass calibration was optimized using a manufacturer recommended multi-element standard consisting of a total of 11 elements (As, Ba, Be, Bi, Ce, Co, In, Li, Ni, Pb, U) at a concentration of 10 μg/L each in HCl. As previously stated, samples and standards were spiked with 10 μg/L In; ^{115}In and ^{75}As were monitored. As will be discussed later, because of initial results, the use of both ^{115}In as internal standard and a three-point (+5, +10, +15 μg/L As) standard addition protocol was adopted for As analysis. Operational parameters for the ICP–MS are shown in Table S2 (SI).

Owens Lake bed dust samples were also analyzed by ICP–optical emission spectrometry (ICP–OES) and by established proton-induced X-ray emission (PIXE) analysis methods [38]. The dust sample was further ground to a silt particle size (20–30 μm) and then pelletized to a 2.5-cm diameter disk against a glass surface. PIXE analysis for a thick target was performed on the samples in vacuum using a Van De Graff style accelerator (Elemental Analysis, Inc., Lexington, Kentucky, USA) run at 2.44 MeV. Samples were irradiated using a 5/8-in. collimator for 10–12 min and the X-rays measured by a Si–Li detector. The calculation of the elemental concentrations in PIXE is based on the X-ray intensity yield that is proportional to specific analyte concentrations. These values are determined by a formula based on reference standards, in the present case the NIST SRM 2711, Montana II Soil, which was pelletized and analyzed under the same conditions during the same run. The pre-pulverization of the samples is intended to reduce sample inhomogeneity issues.

Sample analyzed by ICP–OES were first ground in a synthetic corundum mortar and pestle to a size of ≤30 μm and digested with HNO_3–H_2O_2 as per EPA Method 3050B [39]. For each batch of samples prepared, method blanks and NIST SRM 2711 were also prepared to determine any impurities in the acids used and to check the sample preparation method. The digest was analyzed using EPA Method 6010B [40] on a Leeman Labs direct reading Echelle grating DRE spectrometer. Instrumental operating conditions are listed in Table S3 (SI).

3. Results and discussion

3.1. Samples

We chose three classes of samples: (a) Soil samples supplied by the United States Geological Survey (Denver, CO) that came from various parts of the United States as noted in Table S4 (SI). As noted, half of these had no deliberate arsenic contamination and half had poultry farm litter applied to them. Roxarsone (3-nitro-4-hydroxyphenylarsonic acid) is widely used as a feed additive in the broiler poultry industry to control coccidial intestinal parasites. Poultry farm litter is often applied to soil; it is known that the As rapidly degrades to the inorganic form [41]. The fate and the mobility of the arsenic is also of interest [42]. (b) Soil samples from fallow lands in Murshidabad district in West Bengal, India, a region known to have arsenic contamination of groundwater [10], supplied by the School of Environmental Studies (Kolkata, India). (c) Owens Lake bed dust. Owens Lake, in east-central California, once a thriving water body, dried up due to water diversions in the 1930s to accommodate the water needs of the growing city of Los Angeles. Its dry surface is presently one of the most intense sources of dust in the entire Western Hemisphere, as a result of erosion, lack of vegetation, and high winds [43,44]. Storms can generate dust plumes with an aerosol loading of tens of mg/m^3 [45] with peak arsenic concentrations of 0.4 μg/m^3; dust collected in Owens valley measure 10–50 mg/kg As [46]. There is considerable concern over health effects of windblown dust from Owens lake; a "dustcam" continuously broadcasts a live view [47]. Particle size distribution of our samples is given Table S5 and elemental composition determined by PIXE or ICP–OES is given in Table S6.

3.2. Instrument performance and calibration data

3.2.1. Gas phase chemiluminescence methods

The GPCL method provided statistically indistinguishable calibrations for As(III) and As(V). Either peak height or peak area produce essentially the same linear r^2 value (0.9997 vs. 0.9995) for the calibration curve, the simpler peak height based equation was henceforth used for data evaluation (the uncertainties represent 95% confidence limits):

$$\text{Peak height (mV)} = (169.3 \pm 1.1)\,[\text{As, } \mu\text{g/L}] + 91.0 \pm 30.9, \quad r^2 = 0.9997 \tag{1}$$

Figs. S1 and S2 in SI show the height and area based calibration plots; uncertainties at each concentration are shown therein as ±1 S.D. error bars. Fig. S3 (SI) shows output for triplicate analysis of Owens Lake sample OL3. Based on an S/N = 3 criterion, the LOD was 0.36 μg/L. Spike recoveries on sample extracts were quantitative within experimental error. Direct, rather than standard addition based quantitation was thence used.

The LC–PR–GPCL method also produced linear calibration curves and quantitation was based on height:

$$\text{Peak height (mV)} = (5.855 \pm 0.263)\,[\text{As(III), } \mu\text{g/L}] + 22.2 \pm 12.3, \quad r^2 = 0.9920 \tag{2}$$

$$\text{Peak height (mV)} = (12.020 \pm 0.210)\,[\text{As(V), } \mu\text{g/L}] + 32.5 \pm 9.7, \quad r^2 = 0.9988 \tag{3}$$

$$\text{Peak height (mV)} = (2.339 \pm 0.091)\,[\text{As as DMA, } \mu\text{g/L}] + 1.9 \pm 4.2, \quad r^2 = 0.9940 \tag{4}$$

$$\text{Peak height (mV)} = (2.348 \pm 0.062)\,[\text{As as MMA, } \mu\text{g/L}] + 5.7 \pm 2.9, \quad r^2 = 0.9973 \tag{5}$$

MMA was, however, not detected in any of our samples. A detailed calibration plot with uncertainties at each calibration point is shown in Fig. S4 in SI. The (S/N = 3) LODs were 0.26, 0.13, 0.67 and 0.64 ng As for As(III), As(V), DMA and MMA, respectively. A representative chromatogram is shown in Fig. S5. As with direct GPCL, spike recoveries to sample extracts were quantitative and direct, rather than standard addition based quantitation was used.

3.2.2. Induction-coupled plasma mass spectrometry

Any type of mass spectrometry is susceptible to ionization interference that is matrix dependent. Dilution with a stable isotope that occurs only in trace quantities is the ideal solution but this is not possible for arsenic, a monoisotopic element. From early days

of ICP–MS analysis of As, very many different ways of achieving good quantitation have been advocated for different matrices. In measuring As, Sb, Sn, Bi, Se and Te in Steel, the dual use of ^{9}Be and ^{103}Rh was advocated to bracket the ionization potentials of the analytes of interest [48]. Addition of carbon as methanol or ammonium carbonate was found to enhance ^{75}As signals, which the use of ^{121}Sb as internal standard did not adequately compensate for [49]. In electrothermal vaporization (ETV)–ICP–MS analysis of urine, the simultaneous use of standard addition and ^{121}Sb as internal standard was recommended [50]. For whole blood or urine others had recommended ^{69}Ga [51] as an internal standard, yet others have recommended that 1–3% N_2 be added to Ar, in which case ^{72}Ge, and especially ^{115}In or ^{130}Te work well as internal standards for urinalysis [52]. Unfortunately, for human urine as a matrix, still more recommendations for internal standards abound, e.g., dilution and use of ^{103}Rh [53], ^{193}Ir [54], etc. In other matrices such as wine (both red and white) ^{115}In has been successfully used [55]. For digested nail samples and an Ar–N_2 plasma, ^{130}Te was successfully used [56]. For samples where acid extraction or digestion must be used, varying amounts of acid cause variations in the ^{75}As signal that cannot be compensated for fully by using ^{45}Sc, ^{89}Y or ^{115}In as internal standards; standard addition however leads to satisfactory results [57]. Obviously the recommendations on the best internal standard to use for As analysis are diverse, perhaps even bewildering. We initially tried the use of ^{238}U; this was not very successful, in part because many of our extracts contained this isotope in significant concentrations. Preliminary scans of sample constituents and initial survey led us to settle on ^{115}In. The respective calibration curves were

$$\text{Signal (counts/s)} = (0.983 \pm 0.001)\,[\text{As(III)}\mu\text{g/L}] + 0.399 \pm 0.038, \quad r^2 = 1.0000 \tag{6}$$

$$\text{Signal (counts/s)} = (0.985 \pm 0.050)\,[\text{As(V)}, \mu\text{g/L}] + 3.740 \pm 2.594, \quad r^2 = 0.9922 \tag{7}$$

$$\text{Signal (counts/s)} = (0.998 \pm 0.004)\,[\text{As as DMA}, \mu\text{g/L}] + 0.702 \pm 0.182, \quad r^2 = 1.0000 \tag{8}$$

$$\text{Signal (counts/s)} = (0.902 \pm 0.015)\,[\text{As as MMA}, \mu\text{g/L}] + 1.028 \pm 0.394, \quad r^2 = 0.9994 \tag{9}$$

In direct ICP–MS measurement of inorganic As, Narukawa et al. [58] have recently observed that both ICP–OES and ICP–MS measurements produce a slight but discernible (4%) greater sensitivity for As(V) compared to As(III). A similar statistically significant difference between As(III) and As(V) is not apparent in our data. Whether this was because of use of calibration standards in an acidic matrix or the use of a particular internal standard or just simply different instrument/operating conditions is not known. There is clearly lower response with MMA but the purity of this type of a standard cannot be assured. For inorganic As(III) and As(V), we pooled all data and used a single calibration curve. The results with real sample extracts showed however that internal standard counts varied significantly compared to standards (78–99%) and standard addition of As led to recoveries of 85% on the average. Since we could not assure uniform acidity in the extract due to various degrees of neutralization by the sample and resulting different salinities, we chose the standard addition approach for quantitation as recommended by others [57]. We used a three point standard addition approach to assure data quality. Based on a S/N = 3, the LOD was 0.1 μg/L.

3.2.3. Chloride interference in ICP–MS

In high chloride samples in an Argon plasma, variable background and isobaric interference between $^{75}As^{+}$ and $^{40}Ar^{35}Cl^{+}$ cause problems, this cannot be solved by adding a different As isotope, even if one existed. However, the present samples are not extracted with HCl or NaCl solutions and chloride content of extracts are not particularly high. Matrix interference from chloride that forms $ArCl^{+}$ was studied and is shown as Fig. S6. The fact that the *y*-intercept (the background signal count at *m*/*z* 75, presumably due to $ArCl^{+}$) does not increase systematically with increasing chloride concentration is not obvious in the main plot, this is shown in the inset. In fact even at 100 ppm chloride, the rise in the background counts will only cause a 3% error in the quantitation of 5 μg/L As. But the more important issue and what is obvious in Fig. S6 is that the arsenic calibration slope increases systematically in the presence of chloride. Presumably atomic As is ionized more efficiently by collision with $ArCl^{+}$. Note that 100 ppm chloride concentration in the final extract (the highest value studied here) is tantamount to a chloride concentration of 5 g/kg when 1 g sample is extracted to produce a final extract volume of 50 mL. Majority of agricultural soil samples (non-brackish soil samples) have extractable chloride levels <2 g/kg [59]. The two Owens Lake dust samples that were used for methods intercomparison did have chloride at the 11–12 g/kg level but only 0.4 g amounts of these samples were used for extraction and extract was diluted to 100 mL. Fig. S7 shows treats the 10-ppb standard as an unknown; a three point standard addition plot as practiced in the present work quantitates the unknown with a relative standard deviation of 8.6% for 0–50 ppm chloride concentration and underestimates the actual concentration by ~11%. The presence pf 100 ppm chloride however leads to a 26% overestimation. These limitations of the ICP–MS measurements should be borne in mind when comparing results.

3.3. Sequential extraction

Different extractants and extraction procedures for arsenic extraction from soil have been described in the literature [39,60–62]. It is not clear that there is any uniquely superior extraction procedure—after all, for geological purposes a total digestion may be most appropriate whereas for the purposes of measuring health hazards of inhaled aerosol the amount that is likely to be readily bioavailable is of the greatest interest. Further, most aggressive oxidative digestion procedures destroy original oxidation state information. Microwave digestion is often used for exhaustive extraction, the USEPA recommends digestion with HNO_3–H_2O_2 [39].

Water, citric acid, sulfuric acid, nitric acid have all been used for extracting As from soil samples. It has been noted that sulfuric acid generally extracts much greater amounts than citric acid [60,63]. Fig. 1 shows the sequential extraction results of the three types of samples; the absolute total amounts of arsenic measured in the samples are shown under each bar (representing the total extracted in extracts A, B, etc., as appropriate). These results were all obtained with GPCL. Owens Lake dust samples consist essentially of re-suspended material that used to constitute a lake. Perhaps it is not surprising therefore that on average half of the arsenic is readily extracted by water. There is very little As that remains after water extraction that is extractable by citric acid. What little is measured in the citric acid extract may well be from the previous extractant in the liquid retained by the sediment. Similarly, there is very little arsenic left that is extractable by nitric acid that was not already extracted by sulfuric acid in these samples. In marked contrast, the fallow soils from Murshidabad examined (WB1–WB5) are rain-washed well drained soils where the water-leachable arsenic has apparently already leached and drained. In fact exclusively for

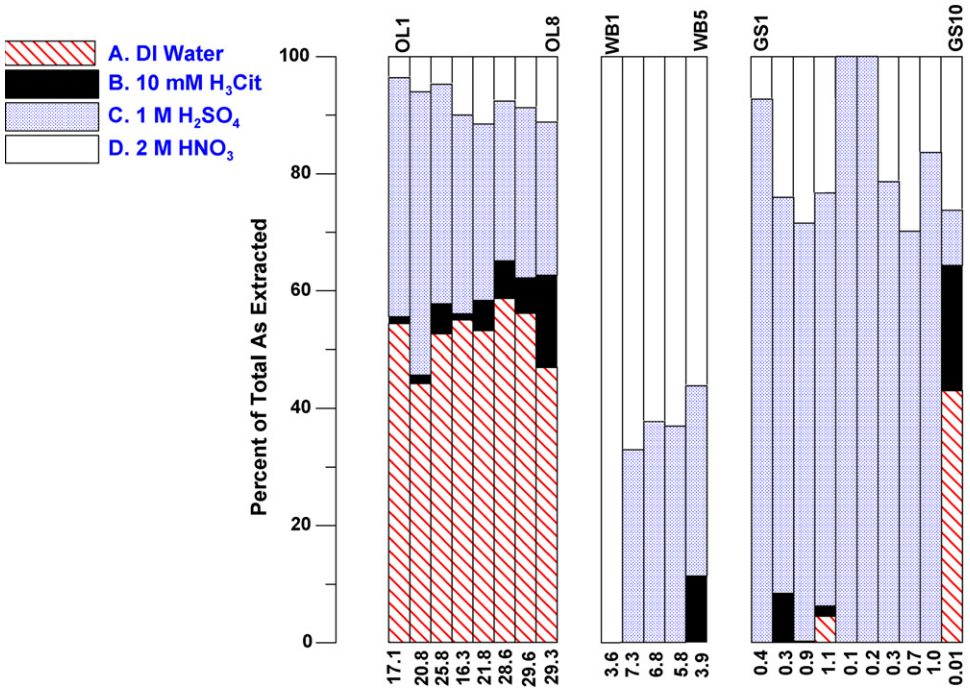

Fig. 1. Fraction As extracted by sequential extraction. Half or more of the As in the Owens lake samples (left group) is water extractable while the soil samples from West Bengal, India (middle group) contain only acid extractable As. The background soil samples from USGS also contain As only in a strong acid-extractable form. The absolute amounts extracted are given in mg/kg below each column. Sample details are given in SI.

WB1, and in general to a major extent for the others, arsenic could be extracted only with the oxidizing acid. The numbers below each bar lists the *total* As extracted. The values for the WB samples are very similar to those reported by Roychowdhury et al. [64] for very similar samples. Note that the Owens Lake samples on the average have 5–6× as much As compared to the samples from WB, India and those have 1–2 orders of magnitude more As than the uncontaminated background soils. Based on the results of repeated extractions with the same extractant (these data are not discussed here), extraction of these samples is likely incomplete and the total As content may be much higher. The arsenic that is extracted comes out most readily in the sulfuric acid fraction. Even in the samples where poultry litter was applied, only As(V) is seen; the same has been observed by others [41,42]. A bar graph depicting the arsenic content (Fig. S8) is given in SI. There is no universal agreement on what the range of arsenic content in typical uncontaminated soil is. While Smedley and Kinniburgh [65] suggest that a range of 1–20 mg/kg is normal for well-aerated uncontaminated soils with limited biological activities, others suggest a much lower "normal" range [66,67].

Despite reasonable efforts at homogenization, small aliquots taken from solid samples are never completely homogeneous. This type of inhomogeneity was particularly apparent in the Owens Lake samples; arsenic concentrations determined in each extract in replicate analysis of the same samples are shown in Fig. S9 in SI. Except for DIW as an extractant with the Owens Lake samples, the amount of arsenic that is extracted by a particular extractant is not necessarily completed in the first extraction; both Figs. S8 and S9 show this.

3.4. Method comparison

A subset of two samples from each class (OL3, OL6; WB4, WB5; GS3, GS6) was chosen for method intercomparison. Initial screening by the LC method showed that As(V) was the only species present in all the samples. For method intercomparison, the intrinsic variability of the arsenic content due to sample inhomogeneity cannot be allowed to play a role. As such, only a sulfuric acid extract, prepared in a sufficient volume to allow analyses by all three methods (ICP–MS) by three point standard addition was examined.

Fig. 2 shows the result of the two present methods against the ICP–MS data. Because blanks were repeatedly run and the results already adjusted to zero, the regression lines were forced through

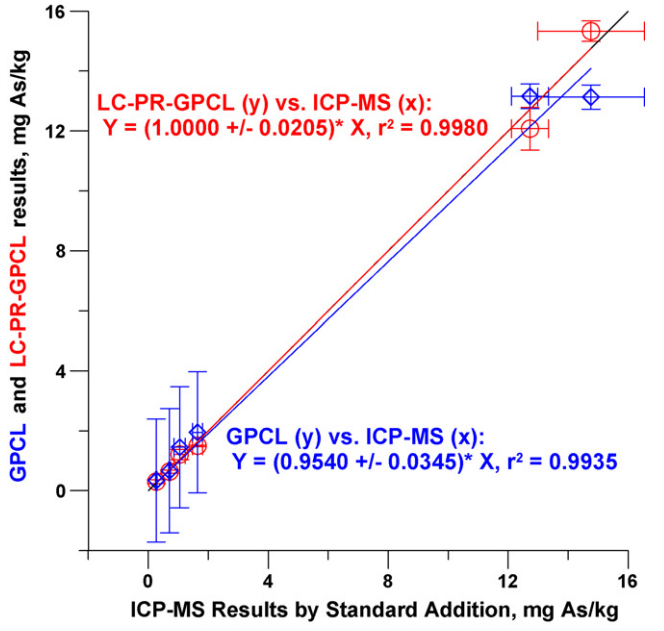

Fig. 2. Regression plots, ICP–MS vs. LC–PR–GPCL (circles) and ICP–MS vs. GPCL (diamonds). Horizontal error bars refer to the ICP–MS measurement, obtained by a three point standard addition method. The 1:1 correspondence line is fully coincidental in this plot with the ICP–MS vs. LC–PR–GPCL regression line.

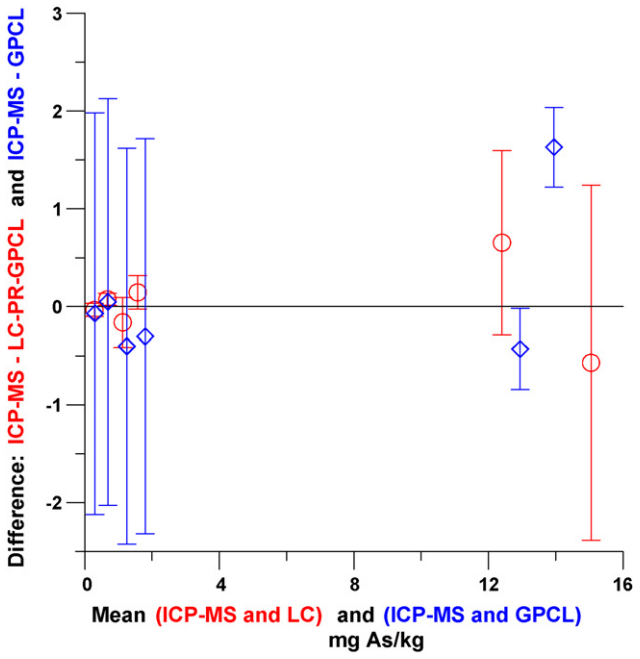

Fig. 3. A difference plot [65] shows no consistent bias for either of the GPCL methods vs. ICP–MS.

the origin. A paired *t*-test cannot take into account standard deviations in the individual measurements which are substantial for the ICP–MS measurements at the high end and for the GPCL measurements at the low end. Still, the ICP–MS and the LC–PR–GPCL methods were indistinguishable at the $p = 0.92$ level while ICP–MS and the GPCL methods were indistinguishable at the $p = 0.82$ level. The linear coefficients of determination are very high and the slopes are indistinguishable from unity for ICP–MS vs. LC–PR–GPCL and nearly so for ICP–MS vs. GPCL. Many believe that a difference plot [68] is of greater help to detect any consistent bias. Such a plot is shown in Fig. 3 and indicates that there is no apparent bias of either method relative to ICP–MS. With soil and dust samples, inherent inhomogeneity is a greater source of uncertainty; this is shown in Fig. 4 for the Owens Lake dust samples where different aliquots were taken for analysis.

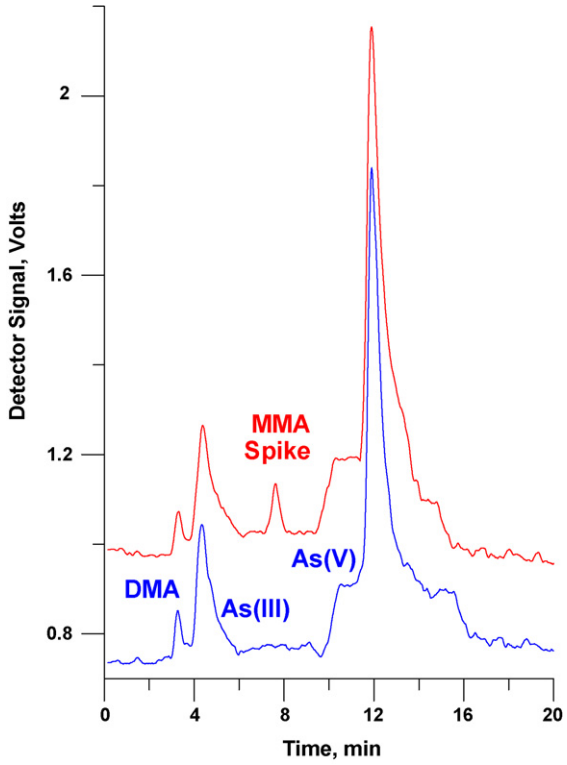

Fig. 5. LC–PR–GPCL analysis of a sample extract (sulfuric acid extract, neutralized). Bottom trace is from the unspiked sample (0.37, 0.45 and 0.70 mg/kg As as DMA, As(III) and As(V), in soil, amounting to 41, 51 and 78 μg/L As in the extract, respectively. The extract was then fortified to a level of 50 μg/L DMA and reanalyzed.

All of the above samples showed the presence of As(V) only. Substantial time had generally elapsed between sampling and analysis and the samples were not stored in a manner that would have prevented microbial activity. Previously we had observed organic As species to be present in stagnant surface water samples [33]. We procured a soil sample from a cultivated field and analyzed this as soon as possible. DMA was present in this sample, but not MMA. A LC–PR–GPCL-based chromatogram of this sample, with and without added MMA is shown in Fig. 5. As analyzed, the unspiked sample extract contained 41.1 ± 4.2, 50.8 ± 0.7, 0.0 ± 0.0

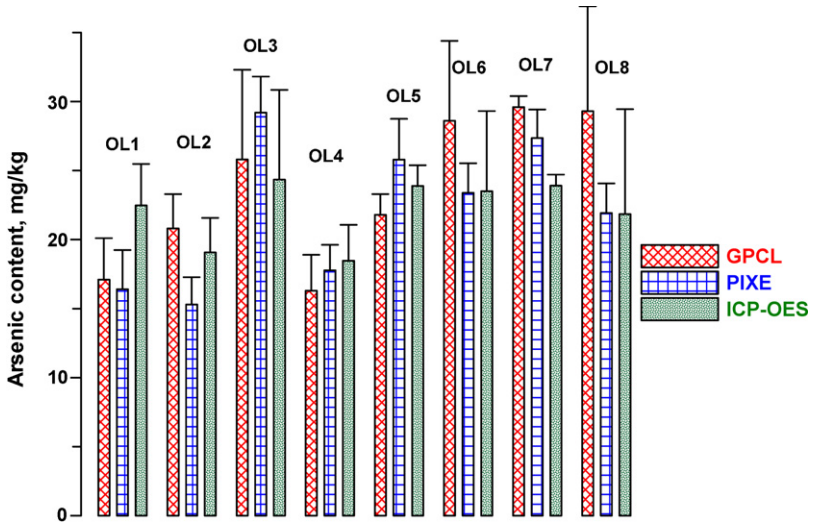

Fig. 4. Owens Lake dust sample arsenic content measured in disparate aliquots by GPCL, PIXE and ICP–OES.

and 78.0 ± 0.7 μg/L As, respectively as DMA, As(III), MMA and As(V). Upon spiking with MMA to a level of 50 μg/L As, reanalysis yielded 42.1 ± 3.3, 48.3 ± 1.3, 51.6 ± 3.3, 78.1 ± 3.0 μg/L As for the same respective species. The same samples were also analyzed by ICP–MS for total As. The spiked and unspiked samples were respectively measured to contain 172.4 ± 0.3 and 220.0 ± 1.7 μg/L As (based on an ICP–MS calibration that contained equimolar amounts of all four As species), compared to the chromatographic sum of 169.9 ± 4.4 and 220.1 ± 5.7 μg/L As. In absolute amounts, the sample contained 0.37 ± 0.04, 0.45 ± 0.01 and 0.70 ± 0.00 μg/g As abs DMA, As(III) and As(V), respectively, clearly indicating the ability of the method to speciate sub-ppm levels of As in soil.

4. Conclusions

The gas phase chemiluminescence method for arsenic analysis is an inexpensive affordable approach that is not only applicable to water, it is applicable to soil extracts and likely, a variety of other sample types after appropriate extraction. Although the reactor has to be manually washed afterwards, it is interesting to note that because the method intrinsically involves matrix isolation, it is capable of handing mud or sediment samples directly. The GPCL equipment costs ∼1% of that of ICP–MS and can reach an LOD within a factor of 4 of the large, expensive instrument. Unlike ICP–MS, there is no chloride interference issue and there are no needs for internal standards or standard addition based quantitation. At a typical consumption rate for argon of 10+ L/min for a typical ICP-based spectrometer, the operating costs are also two orders of magnitude lower. The GPCL technique can be used equally well with and without a chromatographic front end for speciation. It is ironic that all speciation work on samples from South Asia, where the problem is the most acute, has been carried out in fact outside the affected countries. The GPCL technique can bring affordable speciation to many laboratories. We had previously published a complete parts/vendor list [32] and reiterate herein the offer that we will provide assistance to any nonprofit organization interested un building GPCL analyzers for As.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2008.06.037.

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