



## Research papers

# Colorimetrically determining total antimony in contaminated waters and screening for antimony speciation



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## ABSTRACT

A colorimetric method based on the development of the yellow potassium iodoantimonite complex, previously developed for biological matrices, was applied to successfully quantify total Sb in contaminated waters that were collected from an Sb mineralised zone in NSW, Australia. The method showed good repeatability and little interference from co-occurring ions such as As (III),  $\text{Ca}^{2+}$ , Fe (III) and  $\text{SO}_4^{2-}$ . Field testing demonstrated good precisions and recoveries, making the method truly quantitative under the given conditions. The method's detection limit and limit of reporting ( $0.6 \mu\text{g mL}^{-1}$ ), made it applicable in areas of high Sb concentration and for rapid response to Sb contamination. Preliminary investigations into extending the method to rapid Sb speciation screening was trialled using anionic SPE columns that retained Sb (V) and excluded Sb (III), in isolation and in combined solutions. Antimony (V) retention was compromised in the presence of ions such as  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  spiked at realistic field concentrations. Despite this, the coupling of the colorimetric determination with the anionic columns showed no gross interferences during field trialling, and the columns showed potential for rapid screening of Sb species, as well as rapid preconcentration of Sb from water samples. The latter process lowered the effective detection limit of the colorimetric method almost 10-fold. Both the colorimetric method and the combination of this with rapid speciation techniques show great potential for expanding rapid Sb analysis capability, applicable especially for screening water samples with known or suspected Sb content.

## 1. Introduction

Global production of antimony (Sb) from mining has been increasing in recent years, given its numerous industrial uses including as a fire retardant, semi-conductor, and even as a medical agent (Wilson et al., 2010). This group 15 element predominantly occurs as +3 (III) or +5 (V) species in the environment. There is no known human requirement for antimony, which has carcinogenic potential and is known to be clastogenic in its +3 form (Denys et al., 2008; Filella et al., 2002a; Obiakor et al., 2017a; Wilson et al., 2010).

Antimony is analytically problematic. Many laboratory techniques are used for total Sb and its speciation analysis including HPLC-ICPMS, ICP-OES, HPLC-HGAAS, and electrochemical methods such as differential pulse anodic stripping voltammetry (Nash et al., 2000; Quentel and Filella, 2002; Smichowski et al., 1998; Telford et al., 2009). These are often expensive, time consuming and may be quite complex. This can cause problems in situations such as environmental monitoring and spill response (Vanhoof et al., 2013), or in remote areas where the more typical laboratory analyses of Sb are not feasible. In particular, the ability to both rapidly detect Sb in environmental waters, and to have

some preliminary indication of species present, would reduce research and monitoring costs and increase response times while supplementing the environmental information available for this metalloid.

Colorimetric methods exist for Sb determination. In practical terms they range from simple (with 1 or two reagents and analytical steps) to complex (with up to a dozen reagents or analytical steps) and exhibit a range of actual and potential detection limits (from  $\text{ng mL}^{-1}$  to  $\mu\text{g mL}^{-1}$ ) (Christopher and West, 1966; Fauchon, 1937; Fredrick, 1941; Matulis and Guyon, 1965; McChesney, 1946; Rath et al., 1997; Tripathi and Patel, 1998). Thus, while colorimetric approaches have played a very minor role in the analysis and research of Sb in the environment, careful selection, adaption and trialling of a colorimetric method is required to provide the desired ability to rapidly, cheaply and accurately detect Sb under a set of given field conditions.

In natural waters Sb predominantly exists in inorganic form. The Sb (III) species is generally considered to be up to 10 times more toxic than Sb (V) (Luo et al., 2015; Smichowski et al., 1998), but this statement remains contentious (MacPhee and Ruelle, 1969; Obiakor et al., 2017b; Quiroz et al., 2013; Takayanagi, 2001), which illustrates the dearth of information on the behaviour of this metalloid. The Sb species present

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depends on a number of factors including pH, redox, and co-occurring oxidants/reductants within a system. Co-occurring ions (particularly aqueous species of Mn, Al, Fe and Ca) have been shown to influence the mobility and solubility of Sb within the soil-water system by oxidising/reducing adsorbed or precipitated Sb species (Johnson et al., 2005; Wan et al., 2013a; Wan et al., 2013b). Thus, while Sb (V) is typically dominant (often even under reducing conditions) (Mitsunobu et al., 2006) it is difficult to simply infer speciation from environmental conditions. Field based speciation methods have been developed that have been shown to accurately represent the species ratio of elements such as arsenic (As) present at the time of sampling (Watts et al., 2010). The application of such a technique to Sb has not been published, but coupled with a rapid colorimetric approach to Sb quantification, should provide an important move forward in Sb determination for both research and monitoring.

The aim of this study was firstly to assess a simple colorimetric method based on the development of the yellow potassium iodoantimonite ( $\text{KSbI}_4$ ) complex in the presence of Sb (Fauchon, 1937; McChesney, 1946) for the rapid quantification of total Sb in waters with highly variable Sb concentrations (up to  $25 \mu\text{g mL}^{-1}$ ). Secondly, this study aimed to combine this colorimetric method with a field speciation technique to provide a rapid indication of Sb speciation.

## 2. Materials and methods

Experimental procedures were undertaken in two sequences. Firstly, the colorimetric method was assessed in terms of linearity, recoveries, effects of co-occurring ions, and field application. Secondly, the method was coupled with an anionic SPE column for Sb speciation screening and Sb preconcentration.

### 2.1. General colorimetric procedure

A summary of the general colorimetric procedure used throughout this work follows. The potassium iodide (KI) reagent was made by dissolving 5 g of crystalline ascorbic acid and 28 g of potassium iodide in 250 mL of deionised water (for a final concentration of 11.2% w/w) as used by McChesney (1946), adapted from Fauchon (1937). The KI reagent was stable for 1 month and was used within that timeframe. Concentrated  $\text{H}_2\text{SO}_4$  (0.5 mL) was added to 2.5 mL of each standard solution and sample to be analysed (producing a final acid concentration of 9.09%). This was followed by 2.5 mL of the KI reagent. After five minutes to allow full colour development, each sample was read at 425 nm in a Spectro biochrom Libra S11 spectrophotometer (cell length 1 cm). Colour development using this method is stable for 48 h as determined by McChesney (1946). The inclusion of ascorbic acid was found to be essential for colour stabilisation. The yellow colour developed in this method is indicative of the potassium iodoantimonite ( $\text{KSbI}_4$ ) complex. All reagents were analytical grade purity. Deionised water (TKA Micropure, Germany) was used throughout the experimental procedure. All Sb standard solutions and reagents were prepared the day of analysis or the day prior to analysis (with the exception of KI reagent). Antimony (V) and (III) standards were prepared from  $\text{KSb}(\text{OH})_6$  (Sigma-Aldrich, USA) and  $\text{KSbC}_4\text{H}_4\text{O}_6$  (AJAX Chemicals, Australia) respectively using final concentration ranges as referenced in the following sections. All analytical runs included an initial and final calibration curve, a drift sample and blank samples approximately every ten samples.

### 2.2. Initial method assessment

The initial assessments of the colorimetric method focused on linearity of calibration curves, differences in repeatability of Sb (III) and Sb (V) as standard solutions, method detection limits, and Sb recovery and precision.

Linearity was checked using a 'high' range calibration set

(0–25  $\mu\text{g mL}^{-1}$  of Sb (V)) and a 'low' range set (0–2.5  $\mu\text{g mL}^{-1}$  of Sb (V)). Each Sb standard solution was measured in duplicate. To determine the repeatability of the analytical reads for different Sb species, calibration curves were generated from solutions of 0–5  $\mu\text{g mL}^{-1}$  Sb (III) and Sb (V). These solutions were measured in triplicate. The method detection limit (MDL) was calculated from seven replicate analyses of the mid-range standard using the high and low Sb (V) calibration solutions (NEPC, 2013). The MDL was also calculated using the same approach with 0.5  $\mu\text{g mL}^{-1}$  Sb for both Sb (III) and Sb (V) solutions as part of the Sb (III) and Sb (V) repeatability assessment. The limit of reporting (LR) was established at 5 times the MDL (NEPC, 2013). Analytical precision was measured by the relative standard deviation (RSD) which was considered acceptable when less than 10%. Recoveries were calculated for each MDL analysis based on the spiked value and a baseline analytical/instrumental uncertainty was calculated using the instrumental limit of uncertainty and standard error propagation methods as per Skoog et al. (2014) and expressed as a % uncertainty relative to a 0.5  $\mu\text{g mL}^{-1}$  spike of Sb.

### 2.3. Influence of co-occurring ions on Sb quantification

The effect of co-occurring ions on the determination of Sb (at 0.5  $\mu\text{g mL}^{-1}$  of Sb (V)) was tested for Al (0.5  $\mu\text{g mL}^{-1}$ ), As (2.5  $\mu\text{g mL}^{-1}$ ), Ca (500  $\mu\text{g mL}^{-1}$ ), Fe (0.1  $\mu\text{g mL}^{-1}$ ), Mn (2.5  $\mu\text{g mL}^{-1}$ ), and S (550  $\mu\text{g mL}^{-1}$ ). Concentrations of these co-occurring ions were selected based on previous values obtained from adit waters for the Bracken Resources Pty Ltd Hillgrove Antimony/Gold Mine (30°34'S, 151°54'E) approximately 25 km east of Armidale, New South Wales, Australia) to represent median to high, yet realistic values (Picone, 2011). All co-occurring ion solutions were made from commercially provided standards (Australian Chemical Reagents Moorooka, QLD). Aluminium, Fe and Mn standard solutions were made from the respective metals (assumed to be present as  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$  respectively in solution). The As (III) standard was made from  $\text{As}_2\text{O}_3$ . The S and Ca standards were made from  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{CaCO}_3$  respectively and can be assumed to be  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$  in solution. All standards used high purity source materials and were provided in a 2% nitric acid background solution and while assumed to be present initially in the above ionic forms, will be referred to using elemental symbols hereafter, given the reducing nature of the colorimetric method. Tests were undertaken with each single ion, and on 4 combinations of ions using the concentrations above. The first combination of ions contained As, Fe, Mn, S, Al, Ca and S. The second mix contained As, S, Ca. The third contained As and Ca while the fourth contained As and S. Each test was replicated 6 times and values were determined as recoveries of Sb.

### 2.4. Field testing of the colorimetric procedure

Field testing of the colorimetric procedure was undertaken on samples from five old and current mine adits (Sites A, B, C, D and E) at the Bracken Resources Pty Ltd Hillgrove Antimony/Gold Mine. The Hillgrove mineral field is variably comprised of current and historic mine workings associated with stibnite-quartz veins/breccias in meta-sedimentary and granite rocks. The area consists of gorges and plateaus with local relief of up to 300 m from ore processing areas to the valley floors. The mineral field has an intermittent mining and environmental degradation history spanning back to the late 1800s, with several water seepages within the mine lease area containing low to very high concentrations of Sb (up to 50  $\mu\text{g mL}^{-1}$  Sb has been recorded). Further details on the history and environmental context of the Hillgrove Mine and associated historic mine workings can be found in Ashley et al. (Ashley et al., 2006; Ashley et al., 2007).

At each site, approximately 1 L of water was sampled using a 1 L acid washed Teflon bottle following standard field sampling protocols (Standards Australia, 2005). Samples were collected in triplicate at each site and were filtered through a pre-washed 0.45  $\mu\text{m}$  membrane

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