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Review

Electroanalytical Determination of Antimony

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Antimony is an element that is common in the environment owing to numerous industrial applications and, in places, natural occurrence. The toxicity of some antimony compounds ought to place the element at the focus of analytical determination. Electrochemical methods offer a simple approach to antimony analysis, most frequently by use of anodic stripping voltammetry. To-date however, a comprehensive review of the electroanalytical literature has not been reported. Herein electroanalytical determination of antimony is reviewed, along with relevant aspects of its speciation.

Keywords: Antimony, speciation, electroanalysis, metal chelation, stripping voltammetry

1. INTRODUCTION

Antimony is a relatively toxic element that is becoming increasingly common in the environment [1]. Its prevalence is due to a wide range of industrial applications, including use in glass making and ceramics [2], the fabrication of fire retardants [2], lead –antimony alloyed materials in batteries, ball bearings and ammunition [2,3], automobile brake linings [4,5] as well as increased application to the development of microelectronics [6,7]. Owing to its use as a catalyst in the fabrication of polyethylene terephthalate (PET) antimony is invariably found in plastic containers made of this material used for water and fruit juices, and consequently fruit juices have been found to contain antimony levels greater than the EU limit [8-10].

The toxicity of antimony is not yet fully understood with respect to human health or the environment. The element is poisonous to humans and animals at high dosage, with symptoms akin to arsenic poisoning. It is not known to serve any biological function [11], but has been administered in the treatment of certain tropical diseases, as have other toxic heavy metals [12,13]. High exposure can cause nausea and dizziness in the mild case, dermatitis and antimony spots on the skin from prolonged skin exposure, and in the case of acute oral antimony poisoning symptoms include abdominal pain,

vomiting and diarrhoea, the extreme case leading to kidney and liver failure and death [14,15]. Inhalation of antimony is considered a possible carcinogen to humans [15-17], and in recent years antimony compounds have been linked to pervasive developmental disorders such as autism and sudden death syndrome [16,17].

Although it has been reported that trivalent antimony is more toxic than the pentavalent species [18], pollution guidelines for maximum contamination of water and soil systems are considered with respect to the total antimony concentration. At present the European Union holds the lowest maximum permitted level in drinking water of 5 $\mu g\ L^{-1}$ [19], though limits elsewhere range to 20 $\mu g\ L^{-1}$ [20]. Normal concentrations of antimony in groundwater, seawater and surface water range between 0.1 to 0.2 μgL^{-1} (ca. 1 nM) [21], yet concentrations are considerably greater near acid mine drainage and industrial sites.

Despite its toxicity antimony has received very little analytical attention relative to other toxic heavy metals and metalloids. Antimony has four main oxidation states; -III, 0, +III and +V, but predominantly exists in the environment as Sb(III) and Sb(V). In non-polluted waters it is found at concentrations less than 1.0 $\mu g\ L^{-1}$ (nM), invariably in the form of the Sb(V) species (when speciation is conducted) [22]. Lack of information regarding the element is evident in our poor understanding as to the cause of transformation between species, as well as the presence of both antimony III and V despite a thermodynamic preference for Sb(V) in oxygenated environmental samples [22].

In 2002 Filella et al [22,23] composed an extensive review of the scientific literature with a view to identifying and evaluating all analytical data regarding antimony. The review is thorough, and provides an excellent basis for understanding the nature, occurrence, and solution chemistry of the element in natural waters and soils. Furthermore, a more recent review also by Filella et al [24] addresses the "Knowns and Unknowns" of antimony in the environment, concluding that more focused research in required, particularly with respect to speciation analysis and ecotoxicology.

This present review aims to compile and discuss all the literature specifically regarding the *electroanalytical* determination of antimony to date, and critically compare electrochemical methods to alternative analytical approaches. The primary focus is on English language papers found using a number of science based publication search engines, namely SciFinder, Scopus and Web of Science, but to be comprehensive also summarises most of the non-English language research papers found during these searches (see Table 4).

2. ELECTROCHEMICAL DETERMINATION AND SPECIATION OF ANTIMONY

Although a wide range of spectroscopic techniques are available to determine total antimony and the speciation of antimony in real environmental samples (discussed later), the nature of the equipment used for such analysis is often large, bulky, expensive and/or relatively immobile. Owing to the need for smaller, simpler analytical approaches that can be used in the field for in-situ environmental analysis, and at a much lower cost, numerous electrochemical approaches to antimony determination have also been developed. The call for portable, in-field analytical sensors is also necessary owing to concerns regarding sample containment and solution ageing [25,26].

Table 1. Electrochemical determination of antimony using mercury electrodes

Technique	Electrode	Modifier/ Complexing agent	Sb(III) LOD (M)	Sb(V) LOD (M)	Year	Ref.
DP ASV	C SPE MFE		1.27E-08	n/a	2009	39
DP ASV	HMDE		n/a	5.00E-08	2008	112
DP ASV	HMDE		4.60E-07	n/a	2003	113
DP ASV	HMDE		9.00E-11	NR	2002	30
DP ASV	HMDE		1.30E-10	n/a	2000	108
DP ASV	GC-MFE		1.00E-07	n/a	1999	38
DP ASV	HMDE		1.30E-07	n/a	1997	114
DP ASV	HMDE		NR	NR	1997	34
DP ASV	HMDE		NR	NR	1996	35
DP ASV	HMDE		1.00E-08	NR	1995	41
DP ASV	HMDE		1.64E-10	NR	1991	115
DP ASV	HMDE		8.20E-07	n/a	1983	116
DP ASV	HMDE		4.10E-10	n/a	1979	106
DP ASV	HMDE		6.30E-08	n/a	1995	117
DP ASV	HMDE		n/a	n/a	1974	42
LS ASV	HMDE		1.06E-07	NR	1983	105
LS ASV	GC-MFE		2.00E-08	n/a	1985	40
LS ASV	Graphite-MFE		1.60E-09	n/a	1973	118
PSA-CC	GC-MFE		4.90E-09	NR	2007	109
PSA -CC	GC-MFE RDE		6.60E-11	n/a	2010	29
PP	HMDE		6.10E-09	n/a	1968	119
A.C. ASV	HMDE		NR	NR	1979	107
SQW ASV	HMDE		4.00E-07	n/a	2004	120
DP AdASV	HMDE	ARS	1.20E-08	n/a	2008	53
LS AdCSV	HMDE	catechol	2.00E-10	2.00E-10	1987	43
DP AdCSV	HMDE	catechol	NR	2.00E-07	1982	37
DP AdCSV	HMDE	catechol	8.20E-10	n/a	1997	44
DP AdCSV	HMDE	chloranilic acid	2.20E-09	n/a	1999	45
DP AdCSV	HMDE	chloranilic acid	1.70E-09	4.60E-09	1996	46
DPASV	HMDE	chloranilic acid	NR	NR	1998	47
SQW AdCSV	HMDE	gallocyanine	2.00E-09	n/a	2005	121
PSA	GC-MFE	Hg(II) ions	2.50E-09	NR	1998	67
PSA	GC-MFE	Hg(II) ions	7.40E-09	n/a	1995	33
AdCSV	HMDE	morin	7.00E-10	n/a	1998	122
LS AdCSV	HMDE	oxine	1.00E-10	n/a	1991	51
DP AdCSV	HMDE	pyragallol red	9.98E-09	4.87E-08	2006	49
Ad LSV	HMDE	pyrogallol	2.50E-08	8.20E-08	2009	50
DP AdCSV	HMDE	pyragallol	1.03E-10	9.48E-09	2007	48
DP AdCSV	HMDE	TAR	4.06E-10	NR	2011	52
LS AdCSV	HMDE	p-DMPF	1.00E-09	n/a	1995	123

DP – Differential Pulse, **ASV** – Anodic stripping voltammetry, **LS** – linear sweep, **PSA** – potentiometric stripping analysis, **CC** – constant current, **PP** – pulse polarography, **SQW** – squarewave, **AdASV** – adsorptive anodic stripping voltammetry, **AdCSV** – adsorptive cathodic stripping voltammetry, **SPE** – Screen printed electrode, **MFE** – Mercury film electrode, **HMDE** – Hanging mercury drop electrode, **GC** – glassy carbon, , **RDE** – rotating disc electrode, **ARS** – Alazarin Red, **TAR** - 4-(2-thiazolylazo) – resorcinol, **p-DMPF** - p-dimethyl aminophenyl fluorine

Table 2. Electrochemical determination of antimony using carbon and gold electrodes

Technique	Electrode	Modifier/Complexing agent	Sb(III) LOD (M)	Sb(V) LOD (M)	Year	Ref.
CARBON ELECTRODES						
SQW ASV	BDD	IrOx	8.00E-07	n/a	2007	124
DP ASV	C SPE	silver nps	6.79E-10	n/a	2007	27
Ad ASV	CPE	pyrogallol red	1.00E-09	n/a	2005	31
Ad ASV	CPE	bromopyragoll red	5.00E-10	n/a	2004	62
DP AdASV	CPE	phenylfluorone	8.90E-09	n/a	1996	68
PSA	CPE MWCNTs	Hg(II) ions	5.00E-08	n/a	2009	32
SQW CSV	EPPG	bismuth	1.64E-11	n/a	2009	66
SQW ASV	EPPG	bismuth	4.10E-11	n/a	2011	28
DP AdASV	GC	pyrogaloll	4.10E-10	n/a	1998	63
CV AdSV	GC	polyphenols	4.90E-08	NR	2003	64
DPV	GC	SWCNTs/POM	7.00E-07	n/a	2008	65
ASV	GC RDE		1.00E-08	n/a	1975	57
Ad CSV	Graphite	TPMD	3.00E-08	n/a	1974	61
GOLD ELECTRODES						
DP ASV	C SPE Au nps		9.44E-10	n/a	2007	69
ASV	GC-Au film		4.60E-09	n/a	1980	72
DP ASV	GC-Au film		1.60E-09	n/a	2000	73
PSA	GC-Au film		4.10E-05	n/a	1984	70
DP ASV	gold		2.10E-09	n/a	2002	71
PSA CC	gold fiber		2.50E-09	NR	1987	74
PSA	gold tube		1.60E-09	2.60E-09	2007	75

SQW – squarewave, **ASV** – Anodic stripping voltammetry, **DP** – Differential Pulse, **AdASV** – adsorptive anodic stripping voltammetry, **PSA** – potentiometric stripping analysis, **AdCSV** – adsorptive cathodic stripping voltammetry, **CV** – cyclic voltammetry, **BDD** – boron doped diamond, **SPE** – Screen printed electrode, **CPE** – carbon paste electrode, **MWCNTS** – multiwalled cabon nanotubes, **EPPG** – edge plane pyroytic graphite, **GC** – glassy carbon, , **RDE** – rotating disc electrode, **nps –** nanoparticles, **SWCNTS –** single walled cabon nanotubes, **POM** – polyoxomolybdate, **TPMD** – triphenyl methane dye, **NR** – not reported, **LOD** – limit of detection, **M** – moles/L

Tables 1 and 2 present the literature data regarding electroanalytical determination of antimony with respect to the electrode used, the electroanalytical method, modification of the electrode, chelator or solution additive, limit of detection and date of publication. The dates give an indication as to the relatively few research papers spanning over four decades and the direction of more modern approaches. Limits of detection are reported mostly in the nanomolar range, though a number of researchers have reported sub nanomolar limits [27-30].

2.1. Electrochemical techniques

The electroanalytical technique predominantly used in voltammetric analysis of antimony is anodic stripping voltammetry (ASV), frequently in the form of differential pulse (DP) analysis. Detection limits are of the order of nanomolar (μg L^{-1}), often lower, and in many cases speciation of Sb(III) and (V) is reported. ASV methods involve the electrochemical reduction of Sb(III) to Sb(0) at

the electrode surface, cathodically pre-concentrating the metal at the electrode for an optimised time period, and then subsequently driving the electrode anodically to a value beyond the oxidation of Sb(0) to Sb(III).

The stripping peak observed corresponds to the concentration of antimony (III) in the electrolyte. Sb(V) is only electroactive in certain conditions, and cannot be directly analysed using ASV due to the necessary reduction to Sb(III) before reduction to antimony metal. As such, there are no known analytical reports regarding the direct electrochemical response corresponding to Sb(V) reduction to Sb(III), though many report the use of lower pH (stronger acidity) to observe total antimony reduction which is then viable [30-32].

Adsorptive stripping voltammetry (AdSV) has also been described in the literature. In these experiments the antimony is adsorbed onto the electrode surface either directly in the case of mercury electrodes, or via a chelating ligand.

On adsorption of the metal or metal-ligand complex the electrode potential is driven cathodically to observe the reduction of Sb(III) to Sb(0) (Ad-CSV) or is held at a cathodic potential and anodically stripped as previously described (Ad-ASV). The benefit of the adsorption process may only be exhibited in the form of an enhanced cathodic or anodic stripping peak relative to the non-adsorbed process in these instances. In some cases the adsorption process occurs in a solution with the antimony sample, but the electrode, post accumulation, is then removed, rinsed and placed into a fresh electrolyte solution. Here the cathodic potential is applied to reduce the accumulated antimony, and the anodic stripping voltammetry is observed as normal [33].

Another approach to electrochemical determination of antimony has used potentiometric methods, again using a stripping process or characterisation via an ion selective electrode [34]. Potentiometric stripping analysis (PSA) differs to conventional ASV in that the pre-concentrated analyte is re-oxidised by chemical oxidants in the solution or a constant current, as opposed to the electrode driven processes of a potential ramp to positive potentials.

Furthermore, the electrolysis time is measured as the potential change is recorded rather than the current response over a changing potential. Hg(II) ions are a commonly used chemical oxidant, and have been used in antimony determination techniques with and without a mercury film electrode [34,35].

2.2. Electrodes

As very few electroanalytical approaches to antimony determination have been published, the literature may be readily separated into three categories based on the working electrode used; mercury, carbon and gold. Ion selective electrodes are also discussed separately. The data are presented in three tables; Table 1 exclusively reporting published data at mercury electrode, and Table 2 presenting the data on carbon and gold electrodes. Table three then compares ion-selective electrodes. The following sub-sections discuss the literature with respect to the electrode type.

Table 3. Electrochemical determination of antimony using ion selective electrodes

Technique	Electrode	Modifier/Complexing agent	Sb(III) LOD (M)	Sb(V) LOD (M)	Year	Ref.
PA	CPE	TIA-TPT	5.00E-06	n/a	2007	76
PA	CPE	TIA-CP	4.00E-06	n/a	2007	76
PA	CW	HCA-TPP	n/a	1.00E-07	1991	77
PA	CW		NR	1.00E-07	1975	78

PA – potentiometric analysis, **CPE** – carbon paste electrode, **CW** – coated wire, **TIA** – tetraiodoantimonate, **TPT** – triphenyl tetrazolium, **CP** – cetylpyridinium, **HCA** – hexachloroantimonate, **TPP** - 1,2,4,6-tetraphenylpyridinium, **NR** – not reported, **LOD** – limit of detection, **M** – mol/L

2.2.1. Mercury electrodes

It is evident from Table 1 that mercury electrodes have been the most frequently applied to antimony determination. Speciation of Sb(III)/(V) is deemed possible using a mercury electrode due to the inactivity of Sb(V) at the electrode in all but highly acidic, halide containing electrolytes [30-32]. As such, many mercury based electroanalytical approaches to antimony speciation involve the determination of Sb(III) and the *total* antimony concentration, allowing the Sb(V) concentration to be deduced. In stronger acids (ca. 4M or more) and in the presence of a large concentration of chloride ions, the reduction of Sb(V) to Sb(III) can occur followed by Sb(III) to Sb(0) [36]. The reduction potentials are very close however, such that the reduction waves invariably overlap [37]. In perchloric acid solutions however, the two polographic reduction waves are discernible [37].

Mercury film electrodes (MFE) and hanging mercury drop electrodes (HMDE) have been applied to the determination of antimony without any other complexing agent or modifiers in a number of publications [29,30,38,39]. The method entirely depends on the formation of an antimony amalgam with the mercury surface, as is frequently the case with heavy metal determination using mercury. Of these approaches DP-ASV is most frequently used, with slight variation in experimental parameters and electrolyte the only apparent distinguishing factor. Quentel and Filella [30] reported the analysis and speciation of antimony from seawater samples using a HMDE in DP-ASV in which the acidity of the electrolyte was varied to achieve a discriminating parameter. In a related paper to Briner et al [40] DP-ASV was applied to the determination of gunshot residue at a HMDE by Woolever et al. [38]. Waller and Pickering [41] re-evaluated DP-ASV approaches to antimony determination in 1995, yet still concluded that HCl concentration remains the discriminatory factor between Sb(III) and total antimony determination. Bately et al [42] noted however that regardless of HCl concentration, MFE were not responsive to Sb(V) in solution, and that total antimony could only be determined by reducing the entire sample down to Sb(III), unlike the HMDE which responded directly to Sb(V) at high HCl concentrations of 4M.

Mercury electrodes have also been used in the presence of complexing agents to aid speciation and lower detection limits. Catechol [37,43,44], chloronalic acid [45-47] and pyrogaloll [48-50] have

been used by a number of researchers as complexing agents to aid, for the most part, adsorptive stripping analysis of antimony. Catechol was first use by McCrory-Joy and Rosamilia [37] in 1982 towards antimony determination in perchloric acid solutions. A later investigation by Capodaglio at al [43] also used catechol as a complexing agent, developing a distinct experimental protocol to determine total antimony concentration at pH 6. In that publication the procedure involved the application of an amalgam forming pre-concentration step at -1.0 V, followed by a re-oxidation of antimony to Sb(III) at -0.2 V for 20s to adsorb the catechol-antimony complex, and finally the analytical CSV of the bound antimony complex. Whilst McCrory-Joy and Rosamilia claim Sb(V) is determined by their procedure, Capodaglio et al infer that both Sb(V) and (III) are adsorbed and reduced equally, and therefore total antimony concentration is determined. Capodaglio et al's procedure has been repeated by other researchers since [44,51].

Pyrogallol has been used as a complexing agent alongside mercury electrode, with a view to discriminate between the adsorption rate of the antimony (III) and (V) complexes and therefore achieve simultaneous speciation of the antimony concentrations [48-50]. The authors report that $[Sb\text{-}py]^{3+}$ adsorbs immediately onto the mercury surface, and can be reduced to Sb-Hg following the adsorption step in the same solution. However, $[Sb\text{-}py]^{5+}$ can take up to 30 mins to form and adsorb onto the electrode, and furthermore requires a deposition potential of -0.2 V (vs. Ag/AgCl in pH 2 buffer) to first reduce the Sb(V) to Sb(III) [48]. The determination is not straightforward however, and in all instances requires extensive mathematical modeling in the form of multivariant Partial Least Squares regression (MPLS) to establish the species concentrations.

Chloranilic acid was first proposed as a complexing agent for antimony by Wagner et al [46] in a procedure that directly discriminated between Sb(III) and (V) species by means of variation in the AdCSV experimental parameters. They claimed that Sb(III)-chloranilic acid (CA) complex could be pre-concentrated onto the electrode at +0.1 V and reduced at -0.14 V in pH 3 solution, where as Sb(V)-CA complex could be selectively accumulated onto the HMDE at -0.5 V and cathodically stripped at -0.4 V in the subsequent scan. Speciation was achieved first by determination of the Sb(III), and then oxidising the entire solution, determining total antimony in the form of Sb(V). Bond et al [47] used this procedure in a combined determination of DP-ASV and DP-AdCSV analysis of zinc electrolytes, and noted that the Sb(V) response was greatly interfered with by Sb(III).

A number of other complexing agents have been used in AdCSV on mercury electrodes, as is evident in the Table 1.

A very recent publication published by El-Shahawi et al [52] is noteworthy in which 4-(2-thiazolylazo)–resorcinol (TAR) was used. This method also used conventional Ad-CSV, using sodium sulphite as a reducing agent to determine total antimony concentration. It was greatly affected by interference of other ions however. In 2008 an interesting approach with one complexing agent, alizarin red (ARS) and a mercury electrode was employed to quantifiably observe the *oxidation* of an Sb(III)-ARS [53]. Unlike other antimony determinations using a complexing ligand in which the reduction of the antimony in the complex is observed, this method claimed that the ARS complex oxidised at a quantifiably different potential to un-complexed ARS.

2.2.2. Carbon Electrodes

Although control measures are in place to use mercury based electrodes safely, the belief remains that mercury is one of the most toxic of the heavy metals [54], and its industrial and analytical applications are being increasingly phased out, particularly with respect to the application of disposable sensors for environmental and biological analysis of hand-held, portable devices [55,56]. As such, the development of non-mercury based electrodes with as good an analytical ability as mercury is of great scientific interest. Carbon electrodes can provide cheap, disposable (when appropriate), rapidly fabricated, diverse and reliable electrodes, applicable to portable sensing. The nature of carbon conductivity allows the electrode substrate to be readily modified and manipulated to a wide variety of systems and posses high selectivity towards specific analytes. Yet very few publications regarding carbon based antimony sensors with speciation capability have been reported.

A variety of carbon electrodes have been applied to antimony analysis including glassy carbon (GC), carbon paste electrodes (CPE), wax impregnated graphite, boron doped diamond (BDD) and screen printed electrodes (SPEs). Surprisingly, in total, very few publications have been reported as can be seen in Table 2. A number of approaches have used the carbon electrode as a substrate for mercury or gold modification, and as such are discussed previously and below, as they exhibit properties specific to the metal modification. In our search for electrochemical approaches to antimony determination, the application of an unmodified carbon electrode in direct stripping or adsorptive analysis was limited to a single, very early experiment in the 1970's [57]. All the other publications and results shown in Table 2 involve the modification or use of a chelating or complexing agents.

Nghi and Vydra [57] were among the first people to report the application of an unmodified carbon electrode to antimony determination, using a rotating disc glassy carbon electrode in aqueous and non-aqueous electrolyte. They found that under optimum conditions, and using ASV antimony concentrations of 10^{-8} M could be analysed. Other, more recent publications have reported antimony deposition and stripping on carbon electrodes [58,59], yet do not report analysis of the antimony itself, but the application of deposited antimony to enhance the stripping analysis of other heavy metals.

Among the earliest publications regarding antimony determination using carbon electrodes were investigations by Brainina et al [60,61] who used wax impregnated graphite electrodes with triphenylmethane dyes (TPMD) or rhodamine C as chelating complexes in solution. The application of TPMDs was based on their established use in solvent extraction, and therefore their known ability to form ion paired complexes with antimony species. Furthermore, TPMDs discriminately react with antimony depending on the oxidation state, such that only Sb(V) and not Sb(III) forms a precipitate that is adsorbed onto the electrode surface, and then quantitatively reduced. The specific TPMDs used by Brainina et al were Malachite Green (MG), Crystal Violet (CrV) and Methyl Violet (MV). They found that Sb(III) was only detected in the presence of both HCl and TPMD, providing a distinct reduction peak for the element in the appropriate conditions. Overall, the method was able to determine Sb(V) and Sb(III) in aqueous solution to concentrations of 30 nM.

Four of the publications reported in Table 2 for carbon electrodes have used pyrogallol in their system, either as a chelating agent in solution [33,62] or as a surface modification of the electrode prior

to analysis [63,64]. Pyrogallol is a polyphenol substance, and in the publication by Shpigun et al [64], five different polyphenol compounds were assessed as appropriate carbon modifiers for antimony; pyrocatechol, morin, gallic acid, salicylic acid and pyrogallol. Pyrogallol-GC gave the most selective response with respect to interference by Cu(II) and Sb(V) with a high sensitivity towards Sb(III), and was thus applied to Sb(III) determination. Yet pyrocatechol and gave a higher response to Sb(III) at all pH levels tested, but was marred by Cu(II) and Sb(V) intereference. Although the detection limit reported was a 100 fold greater than that reported by Khoo et al [63] also using a pyrogallol-GC, the paper was nonetheless comprehensive and discussed the nature of the phenol radicals and their ability to covalently bond with the graphite surface.

An alternative and elaborate approach to antimony determination was reported by Salimi et al [65] in 2008. They discussed a single wall carbon nanotubes (SWCNT) modified GC electrode which was subsequently modified by electrodeposition by the polyoxoanion, α-$SiMo_{12}O_{40}$. The modified electrode was sensitive to the Sb(III)/(V) redox couple, giving a characteristic response at 0.4 V vs. SCE in pH 1 solution. Using DPV the authors achieved sub-micromolar detection limits for Sb(III) in solution, without electrochemical or adsorptive pre-concentration procedures, and only experienced interference effects from relatively high concentrations of arsenic and Sb(V). Analysis via Sb(III)/(V) oxidation has not been reported elsewhere in the literature, and thus despite the relatively higher limit of detection, the research is of great interest and quite novel.

Two recent papers by Zong et al [28,66] used a bismuth modified edge plane pyrolitic graphite (EPPG) electrode. In two different electrochemical approaches Zong et al used the Bi-EPPG electrode in cathodic stripping analysis observing antimony metal reduction to stibine (SbH_3) [66], and later utilising anodic stripping analysis and quantifying antimony metal oxidation to Sb(III) [28]. Both approaches were able to determine total antimony concentrations to very low detection limits of 16 and 40 pM respectively. The anodic stripping approach involved the in-situ deposition of the bismuth modifier with that antimony, and observed an apparent stripping peak at ca. 0.4 V vs. Ag/AgCl in 2M HCl. The authors included L-cysteine in their solution, claiming its application as a complexing agent, though many reports have utilised the compound as a reducing agent of Sb(V) [34,67]. The peak observed at +400 mV is unusual, as the stripping peak for antimony is generally much lower and in the same region as the bismuth peak. It is tempting to therefore speculate that the observation is in fact the oxidation of Sb(III) to (V), particularly as the potential coincides with that observed in Salimi et al's research [65], rather than the alloying effect of the bismuth and antimony as concluded by the authors.

Carbon paste electrodes (CPE) have been used by a number of authors [33,34,62,68]. Guo [33] and Khoo [68] used similar approaches of adsorptive stripping voltammetry in which the complexing agents of pyrogallol and phenylflurone were in solution with the antimony, and the pre-concentration adsorption step occurred in a separate vessel to the reduction and anodic stripping of the accumulated antimony. The method achieved nanomolar detection limits in all cases. Santos et al [34] used potentiometric stripping analysis (PSA) with a CPE fabricated from MWCNTs. The antimony was pre-concentrated a the electrode using a cathodic potential, and the subsequent re-oxidation of the metal was monitored over time based on the chemical oxidation by Hg(II) ions in the solution. The authors subsequently achieved speciation of the antimony by using L-cysteine to reduce Sb(V) to Sb(III) in the solution, and quantifying the Sb(III) and total antimony concentrations.

Finally, screen printed electrodes (SPE), the most attractive form of carbon electrode with respect to disposability, simple and low cost fabrication and portability, has been applied a number of times to antimony determination by Dominguez Renedo et al [27,39,69]. In three separate systems in which the SPE has been modified with a mercury film [39], gold nanoparticles [69] and silver nanoparticles [27], DP ASV has been applied to achieve low detection limits for total antimony. Of the modifications silver nanoparticles were best, although gold was comparable, both achieving sub-nanomolar detection limits.

2.2.3. Gold electrodes

A number of gold electrodes and gold modified electrodes have been applied to antimony determination, the literature details of which are shown in the second part of Table 2. All the gold systems have been used in the stripping analysis of antimony, including DP-ASV and potentiometric stripping analysis (PSA).

No adsorptive approaches have been suggested thus far according to our literature search. The lowest detection limit reported is marginally sub-nanomolar [69], though it is very close to the other reported limits of detection ranging from 1.6 to 4.6 nM with the exception of a PSA electrode possessing a 41 μM limit [70].

An unconventional approach to antimony determination was presented by Wang et al [71] who used a gold disc electrode to explore underpotential deposition (UPD) of Sb(III) and use 1.5^{th} order DP-ASV analytically. The UPD deposition potential was just -0.1 V, much higher than any stripping voltammetric technique yet explored, thus greatly avoiding a wide range of interfering metal ions that generally co-deposit and strip at similar potentials to bulk antimony e.g Cu(II). Bismuth ions remained a prominent interference however.

Three reports of glassy carbon gold film electrodes applied to antimony determination are shown in Table 2 [70,72,73]. The earliest was the joint determination of As(III) and Sb(III) from copper samples published in 1980 [72]. The method involved separating the arsenic and antimony from the copper using a column of Chelex-100, reducing the eluent with sodium sulphite to reduce all the As(V) and Sb(V) to their +3 oxidation states, and then performing a two-step voltammetric analysis. The stripping analysis used an initial deposition potential of -0.3 V, depositing both arsenic and antimony and observing a combined stripping peak, and subsequently using a more anodic deposition potential of -0.05 V to selectively deposit Sb(III) and observe the lone antimony stripping peak.

The method was successful in determining antimony to 4.6 nM. Tanaka et al [73] also used a gold film modified GC rotating disc electrode with ASV to determine the concentrations of total antimony in steel. DP voltammetry was applied, and the procedure optimised such that a lower detection limit than previously reported of 1.6 nM was achieved. The authors reported severe interference effects by Bi(III), Cu(II) and As(III) however.

A gold fibre [74] and gold film modified GC electrode [70] were used in the PSA of antimony in the 1980s. As previously mentioned, the GC-gold film electrode gave a very poor detection limit of

just 41 μM, however the procedure was the simultaneous determination of Bi(III), Cu(II), Pb(II) and Sb(III), and it is worth recognising the well separated peaks observed from the PSA approach on gold . Stripping was achieved via the gold (III) in the solution behaving both as a GC modifier and an oxidant during stripping.

The gold fiber approach used flow cell technology coupled with constant current PSA, and also addressed speciation using the gold electrode, demonstrating the inactivity of Sb(V) on gold electrodes in a manner akin to on mercury electrodes.

The only gold electrode publication to report a concentration limit for both Sb(III) and (V) was reported in 2007 by Santos et al [75]. Here the authors used a flow cell system in which the sample flowed through the gold tubular electrode. The experimental set up was key to speciation analysis, as well as the conventional alteration of deposition potential and HCl concentration to 5 M to determine total antimony.

2.2.4.Ion-selective electrodes: Potentiometric detection

Finally, another type of electrode that has been explored by researchers is the potentiometric ion selective electrode (ISE), fabricated to be specific to antimony ions, thus immediately imposing an aspect of selectivity. Mostafa et al [76] fabricated two types of carbon paste ISE, each using the tetraiodoantimonate (TIA) anion complex as the antimony component, and cetylpyridinium (CP or triphenyl tetrazonium (TPT) complexes as the cation pairs. The CPE were used as potentiometric sensors, but despite an intrinsic selectivity expected of the electrodes they still exhibited interference effects from Hg(II), Bi(III) and Cd(II). Furthermore the detection limits were much greater than any other electrochemical approach reported here, with values of 4 and 5 μM for TIA-CP and TPT respectively.

In 1991 Sanchez et al [77] reported the use of a coated wire ISE, noting at the time the surprising absence of such electrodes in the literature dedicated to antimony analysis. In fact only one earlier report was found, and since the 1991 publication only the one other antimony ISE discussed above has been published. $SbCl_6^-$ is considered an excellent anion for ISEs owing to both Sanchez [77] and Fogg et al [78] used the compound in their coated wire electrode. Sanchez et al combined the $SbCl_6^-$ (HCA) anion with 1,2,4,6-tetraphenylpyridinium (TPP) cation, coating a platinum wire with the ion pair complexes.

The coated wire ISE electrode was fabricated with durable polyvinylchloride (PVC) membrane, and could be reused for months provided it was kept in an appropriate solution. Overall the ISE electrode gave 0.1 μM detections limits, and only had selectivity issues with Au(III) and Tl(III) which are not common interferants.

More problematic was the response of Cu(II) to hydrolyse the $SbCl_6^-$ complex, but this was controlled by adding Ce(IV) to the reaction solution. The earlier 1975 report by Fogg et al [78] was comparable to the coated wire ISE reported by Sanchez, and achieved comparable detection limits of 10^{-7} M Sb(V).

Table 4. Non-English language publications regarding electroanalytical antimony determination

Method	Electrode	Modification or chelator	LOD Sb (III) (M)	Language	Year	Ref
Ad-ASV	CPE	bromopyragoll red	2.00E-09	Chinese	2004	94-96
Ad-ASV	CPE	alizarin violet	1.60E-09	Chinese	2001	100
Ad-ASV	CPE	pyrogallol red	4.00E-10	Chinese	2001	98
Ad-ASV	CPE	alazarin	4.00E-09	Chinese	2000	99
ASV	CPE	bromopyragoll red	2.00E-08	Chinese	2003	97
PSA	GC	TOPO	4.00E-04	Chinese	1988	90
DPSA	Au film		2.00E-09	Chinese	1990	93
ASV	GC-Au film	sulfhydryl cotton	5.00E-08	Chinese	1986	91
PSA	GC-Au film		1.00E-07	Chinese	1986	92
oscillopolarog	HMDE	BQ	4.50E-07	Chinese	2002	125
polarography	HMDE	pyrogallic acid & Se(IV)	3.28E-08	Chinese	2006	126
PA	ISE		1.00E-05	Chinese	1986	88
PA	ISE		2.20E-06	Chinese	1986	89
ASV	CPE-RDE		4.10E-09	German	1971	101
a.c. ASV	GC-MFE RDE		3.30E-10	German	1985	127
DP ASV	HMDE		1.60E-09	German	1987	128
DP-ASV	CPE-RDE		8.20E-08	Japanese	2005	102
ASV	Graphite-MFE	citric acid	N.A.	Korean	1978	129
ASV	GC		2.50E-10	Russian	1975	130
Ad CSV	Graphite	Rhodamine C	5.00E-08	Russian	1966	60
Ad CSV	Graphite	Rhodamine C	5.00E-08	Russian	1971	86
ASV	Graphite		N.R.	Russian	1975	131
2nd diff.pol	Graphite-MFE		1.50E-11	Russian	1978	84
a.c. ASV	Graphite-MFE		1.00E-10	Russian	1973	83
ASV	Graphite-MFE		4.00E-11	Russian	1975	82
ASV	HMDE		4.00E-08	Russian	1962	132
ASV	HMDE		2.50E-09	Russian	1965	133
ASV	HMDE		N.A.	Russian	1982	134
DP	HMDE		4.00E-08	Russian	1971	135
DPP	HMDE	thioruea	2.00E-09	Russian	1983	80
Polarography	HMDE	thioruea	1.00E-04	Russian	1976	81
Polarography	HMDE		2.00E-08	Russian	1964	136
Polarography	HMDE		N.A.	Russian	1970	137
Polarography	HMDE		1.50E-12	Russian	1976	79

AdASV – adsorptive anodic stripping voltammetry, **ASV** – Anodic stripping voltammetry, **PSA** – potentiometric stripping analysis**, DPSA** – differential potentiometric stripping analysis, **PA** – potentiometric analysis, **DP** – Differential Pulse, **2nd diff.pol –** second difference polorography , **AdCSV** – adsorptive cathodic stripping voltammetry, **CPE** – carbon paste electrode, **MFE** – Mercury film electrode, **HMDE** – Hanging mercury drop electrode, **GC** – glassy carbon, , **RDE** – rotating disc electrode, **ISE** – ion selective electrode, **TOPO** - trioctylphosphine oxide, **BQ** - 7-(1-benzeneazo)-8-hydroxyquinoline-5-sulfonate, **LOD** – limit of detection, **M** – mol/L, **NR** – not reported, **N.A.** – not available

2.2.5. Non-English language publications

A limited body of research with respect to antimony determination has been published in languages other than English, and these papers are consequently often overlooked. In Table 4 the authors have striven to tabulate these data and present the results available. The striking pattern in the results is that much of the early work, predominantly using mercury electrodes, was conducted in the U.S.S.R. and has been reported in Russian, and the more recent non-English publications are dominated by the Chinese language.

A number of publications were presented by Stromberg et al, using polography techniques to determine antimony concentrations, reporting values as low as 1.5 x 10^{-12} M [79]. Toropova et al reported using thiourea as a chelating agent with the HMDE [80,81], observing nanomolar detection limits when coupled with differential pulse polorography. In the 1970s a number of researchers utilised a mercury film modified graphite electrode, with results ranging from 10^{-6} o 10^{-10} M [82-84], depending on the electroanalytical technique applied. Furthermore, already mentioned earlier for TPMDs, Brainina et al report earlier experiments using Rhodamine S as a chelating agent to precipitate Sb(V) from the analyte solution and quantitatively observe its reduction via adsorptive CSV at an unmodified graphite electrode [85-87].

In China work regarding antimony analysis began in the 1980s when ISEs [88,89] and modified GC electrodes [90-92] were applied to the system. The ISEs were relatively poor in their determinations, observing detection limits of micromolar concentration. A trioctylphosphine oxide (TOPO) modified GC electrode also gave very poor detection limits via PSA method, though other PSA approaches to antimony determination were more successful , such as differential PSA at a gold film electrode by Ruan et al [93] which gave a 2 nM limit of detection. Very recently there has been a surge of publications in Chinese using CPEs. The CPEs are in every case modified with either pyrogallol red [94-98] or alizarin [99,100], in which the chelator is either in the analyte solution are mixed in with the carbon paste. Detection limits for the CPEs using adsorptive or normal ASV are generally in the nanomolar range.

A few German publications report the use of carbon electrodes also. A CPE rotating disc electrode was reported to give a 4.1 nM detection limit in 1971 [101] without the aid of a chelating agent. A more recent paper in Japanese by Wantanabe et al [102] also using a CPE-RDE did not achieve such detection limits however, despite using DP-ASV, yet still observed a decent result of 82 nM.

2.3. Speciation and interferences

2.3.1. Speciation

As stated previously, antimony has a number of oxidation states, notably III and V. It is of great importance that the speciation of antimony be studied as well as total antimony concentration determination, as the toxicity and physiological behaviour varies depending on the oxidation state. Analysis of antimony in water samples is invariably focused on the III and V oxidation states [24]. In

45 of the papers reviewed by Filella et al [22] the speciation of Sb (III) and Sb(V) in natural water systems was addressed, and it was found that Sb(V) was in much greater abundance than Sb(III) in oxygenated environments [24]. Studies have reported that Sb(III) will age to Sb(V) in a matter of hours in oxygenated systems depending on the acidity of the solution and the presence of chelating ions [103,104]. It is therefore highly important that analysis discriminate between the oxidation states, and that sampling occur with suitable frequency to account for the probable change.

Speciation of Sb(III)/(V) via electrochemical methods often follows the process of determining the Sb(III) concentration, then forcibly reducing the Sb(V) to Sb(III) using chemical reducing agents, and subsequently determining the total antimony concentration. The Sb(V) concentration is then established by subtracting the Sb(III) value from the total antimony determination. A number of different chemicals have been used to reduce Sb(V) to Sb(III) including L-cysteine [34], hydrazine sulphate [29], sulphur dioxide [105], potassium iodide [73] and sodium sulphite [72]. Sulphur groups are said to readily reduce Sb(V) to Sb(III) forming a strong complex with all antimony available, which is why many sulphur containing compounds are used to achieve soft metal chelation in chelation therapy for heavy metal poisoning [17].

To date, it would seem the direct electrochemical determination of Sb(III) *and* Sb(V) in a single sample has not been achieved without the process of determining Sb(III) and then the total antimony concentration. Mathematical approaches have been suggested by a few authors [48-50] in which the adsorption rate of antimony-pyrogallol (py) complexes are discriminated against owing to the much faster kinetics of Sb(III)-py compared to Sb(V)-py. In Zarei et al's [50] paper, the authors describe a mean centring of kinetic profile ratios. The experimental procedure involves holding the electrode potential sufficiently negative (-0.4 V) for 220s to reduce the Sb(V)-py and/or Sb(III)-py and then perform a cathodic linear sweep from 0 to -0.5 V and observe the accumulated Sb-py reduction. The LSV was repeated over 14 mins at time intervals of 1.5 min, and kinetic profiles of the system were recorded. The authors claimed that speciation was possible without chemically reducing the Sb(V) by mean centering of the kinetic profiles recorded. However, as both Sb(III) and Sb(V) are reduced at the same potential of 200mV, it is difficult to ascertain how the peak current was discriminatory. A separate approach that has been applied by the same authors to UV-vis and voltammetric determinations of Sb-py [48,49] used Partial Least Squares regression to resolve the strongly overlapping signals of Sb(III) and Sb(V).

Salimi et al [65] is the only publication thus far to discuss the electrochemical observation of Sb(III) oxidation to Sb(V). It seems surprising that this direct oxidation as a means to determining Sb(III) concentration in a solution, without pre-concentration, has not been researched more. However, in that particular study, the presence of a redox couple at 0.4 V rather than a single, irreversible oxidation peak, does limit the ability of the method to undergo full speciation of a sample as Sb(V) is readily reduced back to Sb(III), and consequently explains the Sb(V) interference experienced by the authors.

Accurate speciation that truly reflect the ratio of Sb(III) to (V) in natural waters is difficult, owing to the thermodynamic favour to form Sb(V) in oxic waters, and the presence of reducing or kintetically stabilising species in the environment that maintain the Sb(III concentration [22-24]. Sampling can disrupt the ratio of Sb(V) /(III) simply by taking away the natural stabilisers, increasing

the dissolved oxygen or disrupting the sample acidity. Quentel and Fillela [30] noted that an accurate seawater sample must have a stabilising agent such as ascorbic acid added to it immediately so as to preserve the actual amount of Sb(III) present. Treatement so organic samples such a UV irradiation and acidic decomposition completely alter the actual Sb(III)/(V) ratio in their application, and as such only total antimony may ever be determined. Furthermore, a number of publications in Tables 1 and 2 [43,53,76] report the use of EDTA as a heavy metal complexing agent to remove interfering metals from samples, without any regard to complexation of antimony to EDTA.

Speciation remains the focus of a number of publications on the determination of antimony, though these are seldom applied to real water samples. There is also a lack of understanding regarding the nature of antimony species in containment relative to in a natural system. Most voltammetric approaches to antimony speciation focus on the determination of Sb(III) in laboratory control or natural yet spiked systems. Although predominantly performed in HCl solutions, voltammetric determinations are conducted in a variety of electrolytes widely ranging from acidic to alkaline conditions, without any discussion regarding the nature of the analyte in the medium [52,53].

2.3.2. Interferences

Many of the research papers presented in both tables report the interference of multiple elements on the electrochemical determination of antimony. Of these copper, bismuth and arsenic are the most prevalent, and can have severe effects on the determinations but also tin, antimony (V) and lead. Cu(II), As(III) and Bi(III) all deposit and strip at similar potentials; a number of approaches have been employed to limit their influence.

Copper interference is often limited by use of a more anodic deposition potential in ASV techniques. A number of researchers using mercury electrodes in particular have reported the use of a -240 mV deposition potential rather than ca. -400 mV so as to avoid the pre-concentration of copper onto the electrode [106,107]. A potentiometric stripping technique involving a double potential step was recently proposed [29] in which the copper is fully oxidised before the antimony stripping step. Another means of controlling copper interference has been suggested by careful moderation of chloride concentration [108]. In this paper by Gonheim et al, eleven metals were simultaneously determined at the HMDE electrode, and the influence of Cl^- on their deposition and stripping peaks extensively studied. Finally, many researchers have omitted interference by copper by use of a separating column, specifically Chelex-100 [31,47,72,109], passing the sample through the column and analysing the copper free eluent. This is not practical for rapid, portable analysis of antimony samples however.

Antimony (V) interference is usually not an issue owing to the inactivity of the species at all but highly concentrated HCl. However, with the increasing use of complexing agents Sb(V) is becoming an increasing problem in achieving speciation as complexation can be indiscriminate [64]. Bismuth seems particularly problematic with gold electrodes, as highlighted by Wang et al with the UPD deposition approach [71], Tanaka et al with their RDE gold film electrode [73] and Huang et al

using a gold fiber electrode [74]. However, the latter group used potassium iodide to suppress the interference of bismuth, though claimed this did not reduce the Sb(V).

As mentioned above, EDTA has been employed to chelate interfering metals from the sample solution by a number of groups [43,53,76]. However, EDTA is indiscriminate when it comes to chelating metals, and it is not certain that the antimony analyte is not complexed with the agent. Alternatively, Khoo et al [68] indicated that EDTA competitively adsorbed at the phenylflurone modified CPE.

Overall a wide range of metals have been indicated as interferences in electrochemical antimony analysis, yet the electrochemical approach remains the most applicable to multiple species analysis. The research presented also illustrates the variety of approaches taken to avoid such interferences and their evident success without the use (in most cases) of chromatography, solvent extraction and precipitation methods.

3. NON-ELECTROCHEMICAL APPROACHES TO ANTIMONY DETERMINATION

A wide range of analytical techniques are available to determine total concentrations of antimony present in environmental samples. The methods are generally coupled procedures, in which the sample is separated using chromatographic stages, heated to a plasma or reduced to a hydride, and then analysed by an element specific detector (ESD). These different techniques were critically reviewed in an article by Nash et al [110], and their application to speciation discussed in a recent review by Miravet et al [111] but are briefly overviewed below.

The most common means presently used to prepare the sample for spectroscopic detection is via an inductively coupled plasma (ICP). The sample is heated using an ICP formed by electrical energy, which exhibits temperatures in excess of 6000 K. ICP is coupled with element specific detection including; atomic absorption spectrometry (AAS), emission spectrometry (AES), atomic fluorescence spectrometry (AFS), and mass spectrometry (MS). ICP methods provide low detection limits in wide linear ranges, rapidly and in the presence of other elements which may be simultaneously quantified. ICP-MS is especially sensitive, and provides the lowest detection limits of all techniques for aqueous sample, observing 20 ngL^{-1} limits [20]. ICP has been in use for just over a decade, thus prior to this neutron activated analysis (NAA) was extensively used as a means of spectroscopic total antimony determination to the μgL^{-1} level [22].

Hydride generation (HG) has been frequently employed in antimony determination, as well as for numerous other metals. It is also often coupled with AAS, AES, AFS and MS as well as with ICP [110]. Hydride generation involves the formation of the volatile SbH_3, generally using a reducing agent such as $NaBH_4$. HG allows for speciation very easily, as Sb(III) forms the hydride much more readily than Sb(V) over a pH range of 2-9. Once the volatile hydride is formed it is analysed by an ESD generally providing sub μgL^{-1} detection limits and efficient speciation [110].

Speciation using ESD techniques requires separation methods be used prior to analysis. HG may be species selective for Sb(III)/(V) as already mentioned, but ICP methods serve only to excite the sample in preparation for analysis. As such ESD techniques are often coupled with separation

stages such as high pressure liquid chromatography (HPLC), gas chromatography (GC), solvent extraction and precipitation methods [111]. To improve the elution and speciation of antimony in HPLC, complexing mobile phases such as organic acid buffers (tartrate, citrate) and complexing agents such as EDTA have been used [24].

4.CONCLUSIONS

Electrochemical approaches to antimony determination have been reviewed herein. Four comprehensive tables present the reported data available and summarise the results with respect to the working electrode material used. It was noted that antimony determination has predominantly been conducted using mercury electrodes, with emerging research now moving towards a greater variety of carbon based electrodes and gold systems. In our assessment of techniques, the repeated use of anodic stripping voltammetry was noted, and recognised to give the lowest detection limits reported. Furthermore, they are frequently employed in multi-element analysis with very little interference effects on optimisation. Speciation and interference effects are also discussed with respect to electrochemical methods, as well as alternative approaches to voltammetric techniques.

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