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Anodic stripping potentiometric determination of antimony on a combined electrode

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The anodic stripping potentiometric (ASP) determination of antimony on a combined working–auxiliary–reference electrode system is described. The method utilises 3 M HCl as supporting electrolyte and a combined glassy carbon mercury film electrode at an electrolysis potential of -400 mV *versus* Ag–AgCl (1 M HCl) for the reliable determination of ultratrace concentrations of antimony. A detection limit of 0.3 μg l^{-1} and a linear concentration range of 0.3–150 μg/l^{-1} antimony were accomplished under these conditions with an electrolysis time of 10 min. The use of L-cysteine was effective for the reduction of Sb^{V} to Sb^{III} and its subsequent use for the ASP determination of the metalloid. The method was successfully applied to the determination of trace and ultratrace concentrations of antimony in water and orchard leaves samples.

The use of a combined working–auxiliary–reference electrode system for the stripping potentiometric determination of cobalt, nickel and lead was first reported by Jagner *et al.*[1,2] More recently, the use of the combined electrode has been extended to the determination of selenium in biological and environmental materials,[3] and to the simultaneous determination of copper, lead, cadmium and zinc in natural waters.[4] The main advantages of the combined electrode system include simplification of the operation and use of stripping potentiometry and improvement of the portability of the required instrumentation for in-field measurements. The combined electrode also has a distinct advantage of enabling the use of microvolumes of samples, usually 50–500 μl, which is particularly important when only a limited sample volume is available. However, despite the inherent advantages of this electrode system, its use for stripping potentiometric determination is still very much in its infancy. A broader demonstration of its potential for the reliable determination of other heavy metals and metalloids is necessary to encourage its wider acceptance for stripping potentiometric measurements.

In this paper, an anodic stripping potentiometric (ASP) method is described for the determination of trace and ultratrace concentrations of antimony on a combined electrode. Beyond the scope of our previous study on the ASP determination of antimony in solid environmental materials on a conventional three-electrode system,[5] the present study focuses on the determination of antimony in water samples on a combined glassy carbon mercury film electrode (GCMFE). Also, the suitability of L-cysteine, instead of hydrazine sulfate used in the previous study, for the reduction of Sb^{V} to Sb^{III} was investigated for the reliable ASP determination of antimony. The application of the method to water and orchard leaves samples was used to demonstrate its suitability for liquid and solid samples.

Experimental

Instrumentation and glassware

ASP measurements were performed with a computerised Radiometer TraceLab potentiometric stripping system. The electrode system consisted of a combined arrangement of the glassy carbon working electrode and Ag–AgCl reference and auxiliary electrodes, which were immersed in an inner electrolyte (1 M HCl), as previously reported.[3,4] The working GCMFE (1 mm diameter) and Ag–AgCl reference and auxiliary electrodes were combined into a single probe with a ceramic plug to permit ionic conductivity. The combined electrode was mounted on an aluminium frame to permit its free movement and rotation of the sample cell. The cells used for all measurements were Eppendorf sample tubes and only 500 μl of sample were used.

All glassware, Eppendorf sample tubes and polyethylene bottles were filled with an acid mixture containing 1 M HCl and 1 M HNO_3, left to stand for at least 1 week and rinsed several times with Milli-Q water prior to use.

Reagents

All chemicals were of analytical-reagent grade. Milli-Q water was used for all dilutions and sample preparations. A stock solution (800 mg l^{-1}) of Hg^{II} was prepared by dissolving the appropriate amount of mercury(II) chloride in 1.3 M HCl. A stock solution of Sb^{III} was prepared by dissolving antimony oxide in 6 M HCl; hydrazine sulfate (0.01 M) was added to the Sb^{III} standard as an anti-oxidant. L-Cysteine was used, in conjunction with hydrazine sulfate, as the reducing agent. Orchard leaves reference material was obtained from the National Institute of Standards and Technology, while the reference water sample was obtained from Australian Government Analytical Laboratories (AGAL).

Anodic stripping potentiometric measurements

The working glassy carbon component of the combined electrode was cleaned initially by polishing with 5 μm aluminium oxide, rinsed with Milli-Q water and then wiped with lint-free paper. The mercury film was then plated by applying a plating potential of −900 mV *versus* Ag–AgCl to the electrode for 2 min in a solution containing 80 mg l^{-1} Hg^{II}. The GCMFE was reconditioned between measurements in the presence of 8 mg l^{-1} Hg^{II}. ASP measurements were performed using a deposition potential of −400 mV *versus* Ag–AgCl and an electrolysis time of 2 min.

Sample decomposition

Orchard leaves. The dried sample was accurately weighed into a pre-cleaned silica crucible and heated gently on a hot-plate until most of the residual moisture and volatile organic matter had been removed. The sample was then ashed in a muffle furnace for 12 h at 450 °C. The ashed sample was removed from the furnace and allowed to cool. Then, 2 ml of 1 M HCl and 0.02 g of L-cysteine were added before heating again on a hot-plate at 80 °C for 10 min to dissolve the ashed sample and to reduce Sb^{V} to Sb^{III}. The final solution was then transferred into a 10 ml calibrated flask (which contained an appropriate amount of hydrazine sulfate to give a final concentration of 0.02 M) and diluted to volume with Milli-Q water. The sample was diluted 1 + 2 with 5 M HCl prior to analysis.

Reference water. A 1 + 1 dilution of AGAL reference water was made using 1 M HCl. After the addition of 1 g l^{-1} L-cysteine, the solution was covered and heated on a hot-plate at 80 °C for 10 min. The solution was then left to cool and an appropriate amount of hydrazine sulfate was added to give a final concentration of 0.02 M. The treated water samples were diluted 1 + 1 with 5 M HCl prior to analysis.

Results and discussion

Optimisation of anodic stripping potentiometry for antimony on combined electrode

The reliable ASP determination of antimony with the conventional three-electrode system in a mixture of 1 M HCl and 0.5 M NaCl was recently reported.[5] However, the results shown in Fig. 1 (curves c and d) revealed that the sensitivity obtained in this electrolyte for low concentrations of antimony (⩽20 μg l^{-1}) on the combined electrode was relatively poor. This may be due in part to the prevention of the working electrode component of the combined electrode system from the reaction products generated at the auxiliary electrode owing to its isolation from the solution. It is generally known that reaction products such as chlorine can contribute significantly to the stripping rate in stripping potentiometry and, hence, influence the sensitivity of the stripping measurement.[6]

The use of HCl as a supporting electrolyte was therefore considered for more sensitive measurement of antimony on the combined electrode (as GCMFE). In general, the sensitivity of the antimony peak increased with increasing HCl concentration up to 3 M. The observed increase in sensitivity with increasing HCl concentration has been attributed to the complexation of antimony by chloride ions.[7] The use of 0.1 and 1 M HCl as supporting electrolytes for the ASP determination of antimony on the combined electrode gave inadequate sensitivity, particularly at analyte concentrations < 20 μg l^{-1}. On the other hand, optimum sensitivity was obtained for antimony on the combined electrode in 4 M HCl. Similar sensitivity and resolution were obtained for the antimony response in 3 M HCl. The use of 3 M HCl as supporting electrolyte was subsequently adopted for all other measurements, as a compromise between sensitivity and slightly lower acid concentration.

As previously recommended,[5] the use of 8 mg l^{-1} of Hg^{II} as oxidant gave optimum response for the ASP measurement of antimony on the combined GCMFE. More interestingly, the antimony response obtained on this electrode system was, in some cases, up to ten times more sensitive at this mercury concentration than in the presence of higher concentrations, particularly for low antimony concentrations (⩽20 μg l^{-1}). Furthermore, the use of 8 mg l^{-1} of Hg^{II} ions as chemical oxidant yielded a linear concentration range of 0–150 μg l^{-1} for the ASP measurement of antimony on the combined electrode, whereas in the absence of mercury the linear range was limited to between 0 and 50 μg l^{-1}. The dissolved oxygen in 3 M HCl alone is therefore useful as chemical oxidant for the ASP determination of antimony at concentrations ⩽50 μg l^{-1}. Evidently, the addition of Hg^{II} ions is useful in accomplishing a more sensitive measurement and a wider linear concentration range.

Electrolysis potential and electrolysis time

Fig. 2 shows that the sensitivity of the antimony response on the combined electrode decreased with the use of more positive electrolysis potentials. This is expected as the more negatively charged electrode will enable a much higher preconcentration of the Sb^{III} ions during the electrolysis step. Although a previous study[5] in a mixture of HCl–NaCl suggested that the use of an electrolysis potential less negative than −400 mV may cause a positive error owing to the co-deposition of Cu^{II} ions, little or no interference was observed from these metal ions on the antimony response obtained with the combined electrode in 3 M HCl used in this study.

The use of an electrolysis potential of −500 mV gave two well resolved peaks for antimony in the presence of a 50 fold amount of copper, as illustrated in Fig. 3. The shift in the peak potentials of copper and antimony is attributed to the complexation of these elements by chloride and as a result they are more

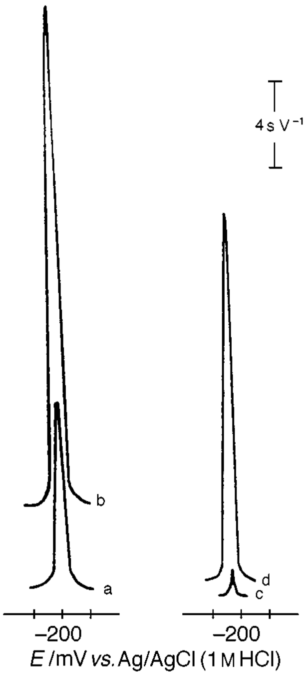

Fig. 1 Influence of supporting electrolyte on antimony response on the combined GCMFE. (a) 20 μg l^{-1} Sb in 3 M HCl, (b) 100 μg l^{-1} Sb in 3 M HCl, (c) 20 μg l^{-1} Sb in 1 M HCl–0.5 M NaCl and (d) 100 μg l^{-1} Sb in 1 M HCl–0.5 M NaCl. E_{dep}: −400 mV *versus* Ag–AgCl (1 M HCl); t_{dep}: 2 min; [oxidant]: 8 mg l^{-1} Hg.

easily resolved.[7] The use of an electrolysis potential of −450 mV resulted in a considerable reduction of the copper peak and the response was totally eliminated with the use of −400 mV, as shown in Fig. 3. All ASP measurements of antimony on the combined electrode in 3 M HCl were therefore performed with an electrolysis potential of −400 mV.

Fig. 4 illustrates the influence of electrolysis time on the sensitivity of the antimony peak on the combined electrode in 3 M HCl. The response for antimony increased with increasing electrolysis time, resulting in saturation at 20 min. In contrast, the use of a conventional three-electrode system did not result in electrode saturation until an electrolysis time of 40 min had been used.[5] The observed difference may be due to the considerable difference in the size of the two working electrodes. The diameter of the previous working electrode was 3 mm, whereas that of the combined electrode was only 1 mm.

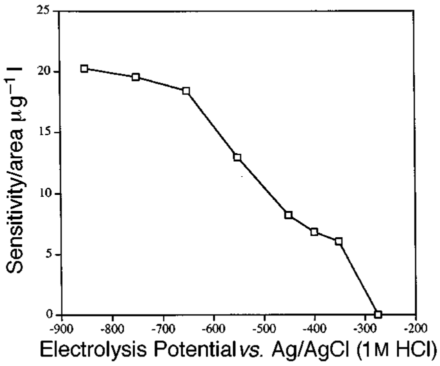

Fig. 2 Influence of electrolysis potential on the sensitivity of the antimony response. 3 M HCl, t_{dep}: 2 min; 8 mg l^{-1} Hg.

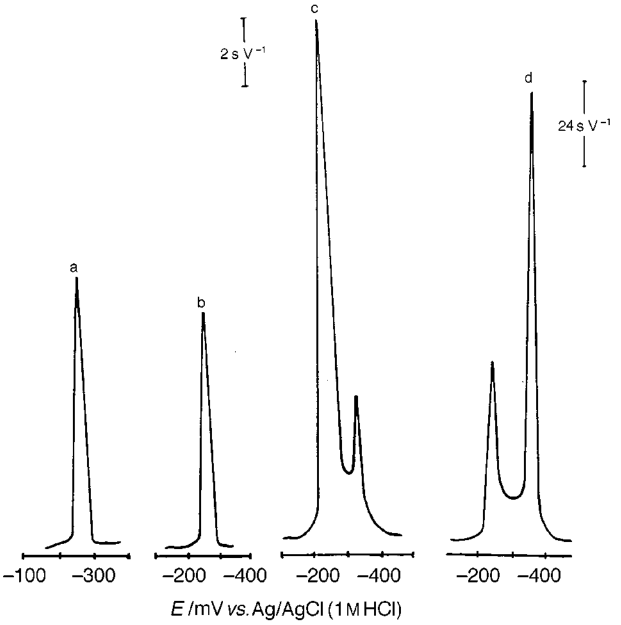

Fig. 3 Effect of copper on antimony response at different electrolysis potentials. (a) 20 µg l^{-1} Sb; E_{dep} −400 mV *versus* Ag–AgCl (1 M HCl); (b) as for (a) + 1 mg l^{-1} Cu; (c) same as (b); E_{dep} −450 mV *versus* Ag–AgCl (1 M HCl); (d) same as (b); E_{dep} −500 mV *versus* Ag–AgCl (1 M HCl). Other conditions as for Fig. 2.

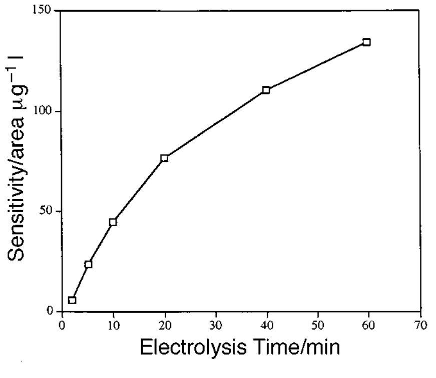

Fig. 4 Influence of electrolysis time on the antimony response. 10 µg l^{-1} Sb; 3 M HCl; E_{dep}: −400 mV *versus* Ag–AgCl (1 M HCl); 8 mg l^{-1} Hg.

A detection limit of 0.3 µg l^{-1} with 9% RSD was obtained on the combined electrode with a 10 min electrolysis time. It is interesting that this detection limit is lower than that (0.9 µg l^{-1}) obtained with the conventional three-electrode system.[5] This may be due to the improved performance of the GCMFE in the absence of reaction products from the auxiliary electrode with the combined electrode design. Further improvement in the detection limit may be accomplished by use of a longer electrolysis time or a more rapid stirring rate.

The achievable linear concentration range for antimony on the combined GCMFE was influenced by the HCl concentration. Generally, the linear concentration range decreased as the concentration of HCl increased (Table 1). This may be due to the ease of formation of chloro complexes with antimony and the more rapid saturation of the electrode at high chloride concentrations $\geqslant$2 M. This view is supported, as given in Table 1, by the much higher sensitivity obtained for antimony at the higher HCl concentrations.

Analytical applications

Inorganic and organic interferences observed for the ASP determination of antimony on the combined electrode were identical to those previously observed on the conventional three-electrode system.[5] Organic interferences are readily eliminated by UV irradiation prior to the stripping potentiometric measurements on the combined electrode.[5,8] Alternatively, the interference of organic substances can be removed by use of suitable sample decomposition methods such as wet digestion or dry ashing. The suppressive interference or enhancement effect of most inorganic substances can be compensated for by use of the standard additions method for quantification.

As the proposed ASP method only detects Sb^{III} on the combined electrode, the reduction of Sb^{V} to Sb^{III} is necessary prior to the measurement. Substances that have been used for this purpose include hydrazine sulfate, sulfur dioxide and a combination of sodium thiosulfate and potassium iodide.[9–13] The use of L-cysteine to reduce and stabilise antimony in solution, as well as to decrease transition metal interference and complex copper ions, has been reported.[14,15] In this study, the effectiveness of L-cysteine in reducing Sb^{V} to Sb^{III} prior to the ASP measurement on the combined electrode was investigated. Table 2 shows the effect of increasing L-cysteine concentrations on the amount of antimony found in the reference water sample by anodic stripping potentiometry. The use of increasing concentrations of L-cysteine gave lower concentrations of

Table 1 Influence of HCl concentration on the sensitivity and linear concentration range of the antimony response

[HCl]/M	Linear concentration range/µg l^{-1}	Correlation coefficient	Sensitivity/area µg^{-1} l*
0.1	0–300	0.993	0.2
0.3	0–300	0.965	1.2
0.5	0–300	0.962	0.3
1.0	0–200	0.983	0.3
2.0	0–150	0.990	2.3
3.0	0–150	0.998	7.8
4.0	0–150	0.995	8.9

* Values obtained at [HCl] < 2 M are affected by poor reproducibility.

antimony in the water sample. This may be due to the interference of excess L-cysteine with the electrode process. The highest antimony concentration found in the water sample was obtained with the addition of 1 g l^{-1} L-cysteine, followed by heating at 80 °C for 10 min. The antimony concentration (271 ± 12 μg l^{-1}) found by reducing Sb^{V} to Sb^{III} with 1 g l^{-1} L-cysteine is close to the certified value (289 ± 29 μg l^{-1}) of the water sample.

Fig. 5 shows that the addition of 2 g l^{-1} L-cysteine is also effective for the ASP determination of antimony in solid samples on the combined electrode. The antimony concentration found in the orchard leaves sample (2.5 ± 0.2 μg g^{-1}) agreed favorably with the certified value (2.9 ± 0.3 μg g^{-1}). Evidently, the required amount of L-cysteine for the reduction of Sb^{V} to Sb^{III} increased with increasing amounts of antimony in the sample. The successful application of the method to the reliable ASP determination of trace and ultratrace concentrations of antimony in the two different types of sample suggests that it may also be applicable to other liquid and solid samples. It is worth noting, however, that when applied to solid samples with high chloride contents, the use of an ashing aid, such as magnesium nitrate, may be necessary to avoid partial loss of antimony during sample decomposition.

Table 2 Effect of amount of L-cysteine used on the antimony concentrations found in certified reference water by anodic stripping potentiometry on the combined electrode*

[L-Cysteine] used/g l^{-1}	[Sb] found/μg l^{-1}
10.0	178 ± 22
2.5	198 ± 16
1.0	271 ± 12

* n = 3; error quoted as mean deviation. Certified value for reference water: 289 ± 29 μg l^{-1}.

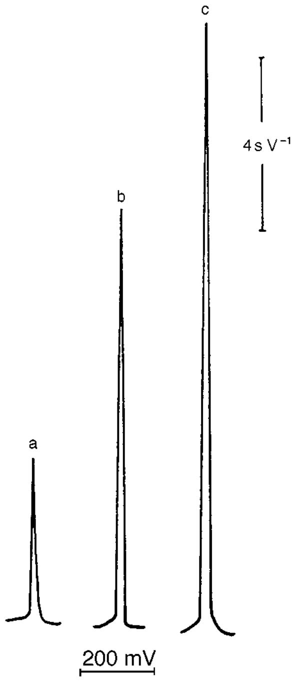

Fig. 5 Quantification of antimony in dry-ashed orchard leaves using the standard additions method. (a) Orchard leaves; (b) as for (a) + 10 μg l^{-1} Sb; (c) as for (a) + 20 μg l^{-1} Sb; 3 M HCl; E_{dep}: −400 mV *versus* Ag–AgCl (1 M HCl); t_{dep}: 2 min; 30 mg l^{-1} Hg. Peak potential: 130 mV *versus* Ag–AgCl (1 M HCl).

Conclusion

The reliable determination of antimony on a combined GCMFE by anodic stripping potentiometry has been successfully demonstrated. Under the optimum conditions, as little as 0.3 μg l^{-1} was detected with an electrolysis time of 10 min. The use of L-cysteine was effective for the reduction of Sb^{V} to Sb^{III} and its subsequent use for ASP determination of the metalloid. The method was successfully applied to the determination of antimony in water and orchard leaves samples.

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