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Electrochemical Method for the Rapid on Site Screening of Cadmium and Lead in Soil and Water Samples

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Abstract Rapid field-based screening methods for the semi-quantitative determination of heavy metals are desirable to support the increasing demand for the rapid characterization of contaminated sites. Single-use sensors have been fabricated using low-cost screen-printing (thick film) technology. These electrodes, coupled with differential pulse anodic stripping voltammetry (DPASV), have provided a rapid, inexpensive on site screening device for the simultaneous field-based determination of cadmium (Cd) and lead (Pb) in soil and water samples in the microgram per litre/kilogram range. A simplified soil extraction procedure, using 1 mol l^{-1} aqua regia and a 3 min ultrasonic sample agitation, has been developed to allow field-based device usage. Extraction efficiency was evaluated using a soil certified reference material (CRM). Recoveries of 64% and 52% for Cd and Pb respectively were obtained, with a relative standard deviation (RSD) of <8% for both analytes (n = 10). Soil samples (82) were tested using the combined extraction-DPASV procedure and compared against standard ICP-AES analysis. Correlation coefficients of 0.9782 and 0.9728 for Cd and Pb respectively demonstrate good correlation between methods. Analytical data is also reported for copper (Cu), but significant peak distortions reduce the confidence of the method for this metal. Results indicate that the combined extraction-DPASV method yields semi-quantitative data for rapid field-based site screening purposes.

Keywords anodic stripping voltammetry · extraction · field-based analysis · monitoring · screening · screen-printed electrodes

1 Introduction

Heavy metals are considered as important environmental pollutants due to their non-biodegradable, persistent and toxic nature. As such, environmental legislation has become increasingly stringent, with growing numbers of samples being submitted for quantitative analysis for routine monitoring or risk and sustainability assessment applications (Pollution Handbook, 2003; Sastre, Sahuquillo, Vidal, & Rauret, 2002). Analysis is generally performed in centralised laboratories using sensitive and accurate but expensive and time-consuming spectrometric techniques. In contrast, field-based analytical methods can minimise delays and potentially reduce costs whilst supporting

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legislation with respect to rapid site characterisation and assessment, monitoring of remediation processes and the enforcement of quality standard regulations on heavy metals discharge. For example, monitoring performance of waste treatment equipment to detect either malfunction or end-of-pipe analysis to ensure legislative compliance is best served using immediate decision making tools. Thus, the development of analytical methods for rapid on site measurements is of increasing importance. Such methods should be used for 'screening' purposes, allowing samples containing specific analytes at concentrations above a pre-set value to be 'filtered out', thereby substantially reducing the number of samples being sent for more expensive and slower, but more precise and accurate conventional analysis (Valcarcel, Cardenas, & Gallego, 1999). The site characterisation specialist must make the choice between the less accurate and precise but reduced cost and improved logistics offered by on site screening compared with the slower and higher cost but improved accuracy and higher precision offered by centralised inflexible laboratory methods. The benefits of rapid real-time data are invaluable, and it could be argued that these benefits far outweigh issues regarding the level of precision and accuracy obtained. The site manager is concerned with determining whether a certain action is required, not the level of accuracy obtained compared to standard methods.

As a result a range of portable instrumentation has being developed. These include lased-induced breakdown spectroscopy (LIBS), immunoassays and X-ray fluorescence spectrometry (XRF). Whilst these methods have specific advantages; most suffer from sample matrix interferences, inherent with simplified field technologies. Matrix interference errors are associated with the measurement technique itself resulting from differences between compositions of calibration standards and samples. The interaction between the analyte with the matrix and the possibility of co-extraction of interfering substances can often lead to signal depression (loss of analyte). The composition of samples, particularly soils is very variable leading to a large number of possible interferents, the exact nature of which is difficult to predict since soils are complex systems with physical and chemical and biological characteristics that vary over time and space (Table I).

This usually results in higher limits of detection and less precision compared to complex laboratory techniques. Other disadvantages may include cost of instrumentation and the need for highly skilled personnel. Voltammetric techniques may at times exhibit sample matrix interferences, however offers a cost effective alternative approach to field based analysis.

Anodic stripping voltammetry (ASV) coupled with screen-printed electrodes (SPEs) offers a convenient technique for on site analysis, for reasons of cost, simplicity, speed (<4 min), sensitivity (μg l^{-1}), portability and simultaneous multi-analyte capabilities (Esteban & Casassas, 1994; Wang, 1994a). SPEs, which operate by application of a sample droplet applied to the electrode assembly, replace classical

Table I Field based screening techniques

Technique	Advantages	Disadvantages	Reference
Lased-induced breakdown spectroscopy (LIBS)	No sample preparation required, analysis of both conducting and non-conducting solid and gaseous samples, multi-analyte analysis	Interference from sample components, availability of suitable standards, sensitivity is less than solution techniques typically 0.1–100 ppm, use of laser increases complexity and cost of instrument, possibility of ocular damage by the high energy laser pulses	Hou and Jones (2000), Hunter, Wainner, Piper, & Davis (2003)
X-ray fluorescence spectrometry (XRF)	No or little sample preparation, multi-analyte analysis, fast analysis, recognised method for detection of Pb in paint USEPA method #6200	Higher limits of detection typically ppm level, need for handling precautions due to the radioactive source, require thin sample, interferences from sample matrix, cost of instrument	EPA method #6200, Kebbekus and Mitra (1998)
Immunoassays	Fast analysis, low cost, simple operation, high sensitivity and selectivity	Lack robustness including short shelf life and reproducibility	Wang, Tian, & Rogers (1998a), Blake et al. (2001)

bulky electrochemical cells, eliminating the associated cumbersome handling, sample de-aeration and lengthy cleaning procedures (Galan-Vidal, Munoz, Dominguez, & Alegret, 1995; Hart & Wring, 1994, 1997; Honeychurch & Hart, 2003; Wang, 1994b; Wang, 2002; Wang, Tian, Nascimento, & Angnes, 1998b). ASV is the most popular electrochemical stripping method for the determination of trace metals, due to the built-in pre-concentration step, lowering detection limits and the ability to measure four to six metals simultaneously. Other methods include cathodic stripping voltammetry, adsorptive stripping voltammetry, and potentiomeric stripping voltammetry (Wang, 1994a). Commercial ASV single metal analysers are available for the detection of Pb or Cu (Electrascan, Eutech Cybernetics, Singapore; SA-1000 scanning analyser, Pailintest Ltd, USA). For background information on ASV and SPEs refer to Wang (1994a) and Galan-Vidal et al. (1995).

ASV coupled to SPEs has been widely studied for the detection of Pb and Cu using a variety of electrode designs and experimental protocol (Choi et al., 2001; Desmond et al., 1998; Kadara, Newman, & Tothill, 2003; Palchetti, Cagnini, Mascini, & Turner, 1999; Yarnitzky et al., 2000; Zen, Chung, & Kumar, 2000). However, no studies to date have demonstrated a device capable of simultaneous metals determination using a range of 'real' soil and water samples, whilst keeping electrode design, fabrication techniques and analytical procedures simple and inexpensive. Furthermore, suitable on site soil sample preparation methods, essential for field implementation, and demonstration in the field using portable instrumentation have not been adequately addressed.

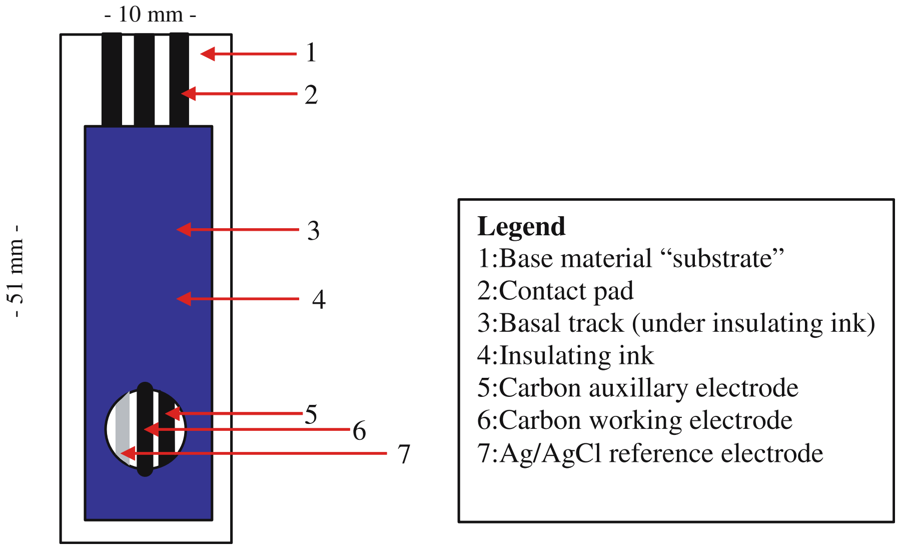
For the first time, an in-depth study of the practical issues of the field-based usage of SPEs for the rapid screening of multiple-metals in 'real' soil extracts and water samples, making use of simple, rapid stripping protocols and minimal reagents is presented. Although an extensive catalogue of laboratory based extraction schemes are available (Kennedy, Sanchez, Oughton, & Rowland, 1997), a technological gap is evident concerning simple, inexpensive and rapid on site metal extraction schemes from soil, which can be easily modified by the end-user, and are suitable to use with this type of device. Such a simplified soil analyte extraction procedure is reported here, offered as a basis for further studies in this important but neglected area. Lastly, field-generated data obtained at a contaminated mining site is presented. The results indicate that the extraction-ASV assay developed yields data that can be used for rapid field-based site screening purposes.

2 Experimental Section

2.1 Electrode fabrication

Screen-printed electrodes (Figure 1) were fabricated in-house by a multi-stage screen-printing process using an automated DEK 248 machine (DEK Ltd,

Figure 1 (a) Carbon SPE; 1 – polyester substrate; 2 – electrical contact; 3 – basal tracks; 4 – insulating layer; 5 – carbon counter electrode; 6 – carbon working electrode; 7 – Ag/AgCl reference electrode. (b) Principle of ASV.



Weymouth, UK) and screens with appropriate stencil designs (DEK Precision Screen Division). Fabrication involved the sequential deposition of multiple ink layers onto surface-treated polyester sheets (ST725; 228 × 305 mm; 0.25 mm thickness; Cadillac Plastics Ltd, Swindon, UK). The basal tracks for the three-electrode system were printed with carbon ink Electrodag 423 SS (Acheson Colloids, Plymouth, UK), providing the electrical contacts and both working and counter electrodes. Silver/silver chloride (Ag/AgCl) biosensor grade C2DR15 ink (15% w/w silver chloride; MCA Services, Cambridge, UK) was used to form the reference electrode. Between printing steps, the layers of ink were dried at 60 °C for 2 h. The three-electrode system was insulated by overprinting an epoxy-resin based polymer insulating ink 242-SB (Agmet ESL, Europe), leaving a defined circular working area (3.2 mm^2) for electrochemical measurements (Figure 1). The electrode strip was heat treated at 120 °C for >2 h to cure the epoxy resin. The compact design allows the fabrication of 100 electrodes per substrate sheet, straightforward connection to the electrochemical analyser using standard connectors (RS Components, UK) and easy and uniform addition of sample droplets onto the three-electrode working area.

2.2 General reagents

All chemicals were of Analar grade, from Sigma Chemical Company (Poole, UK), and Aldrich Chemical Company (Gillingham, UK). Solutions were prepared using HPLC grade water. Cd^{2+}, Pb^{2+}, and Cu^{2+} Spectrosol inductively coupled plasma (ICP) standard solutions (1 g l^{-1}) were used to prepare mixed working standards, diluted to the appropriate concentration using 100 mM potassium chloride (KCl) and 1% v/v nitric acid (HNO_3) as supporting electrolyte.

2.3 Apparatus

Differential pulse anodic stripping voltammetry (DPASV) experiments were performed using a computer controlled Autolab PGSTAT-10 with a general-purpose electrochemical software operating system (GPES3; Eco Chemie, Utrecht, NL). Field experiments were performed using a hand-held PalmSens electrochemical analyser (Palm Instruments BV, Utrecht, NL), this provides 6–8 h of operation using rechargeable batteries and fits into a briefcase.

2.4 On site extraction procedure

Soil (1 g) was weighed into a small acid resistant vial and 5 ml of 1 M aqua regia added (3:1 HCl/HNO_3, HCl 32% v/v, HNO_3 65% v/v), the HCl adding the chloride ions necessary for stabilisation of the Ag/AgCl reference electrode potential. This sample/acid ratio is recommended by the Official and Standardised Methods of Analysis (Watson, 1994). Samples were manually shaken for 3 min (or ultrasonication where indicated). Resulting extracts were filtered using 0.2 μm cellulose nitrate membranes (Whatman, Maidstone, UK) and diluted to 50 ml using high purity water. A Millipore sterifil aseptic filtering system (Millipore, Watford, UK), supplied with a syringe pump to facilitate field use, was used for all sample filtering. Samples were diluted as necessary using supporting electrolyte.

2.5 Electrochemical procedure

The principle of anodic stripping voltammetry is well known. The differential pulse waveform was applied to enhance the signal-to-noise ratio by minimisation of non-faradaic current. DPASV was performed by placing a 100 μl sample droplet on the electrode working area. Each experiment was carried out using a new electrode strip in non-deaerated and unstirred solution (dissolved oxygen did not affect sensor performance). All standards, blank controls and samples were spiked with mercuric nitrate to a final concentration of 200 μg l^{-1}. Co-deposition was performed at a deposition potential (E_{dep}) of −1.1 V for 165 s deposition time (t_{dep}). After depositioning, the potential was scanned to −0.2 V (E_{scan}: $-1.1\ V \rightarrow -0.2\ V$ [pulse amplitude 50 mV, step potential 5 mV, period 0.5 s, hence scan rate of 10 mV s^{-1}]). All data reported represent the mean of three replicate measurements unless otherwise stated. Final analyte concentrations in soil (μg kg^{-1}) and water (μg l^{-1}) samples were calculated by direct calibration.

2.6 Aznalcollar samples and standard methods

Nine soil samples, a sediment sample, two soil certified reference materials (CRM) and four mine water samples were supplied ‘blind’, that is, without pre-knowledge of analyte concentrations (SENSPOL, 2002). CRM 601 was from Flumendosa Lake, Italy (certified acetic acid extract for BCR-SES by Community Bureau of Reference). CRM MR6 was from the Aznalcollar site (Seville, Spain) certified for pseudo-total metal content (Laboratory of Reference Materials, Dept. Analytical Chemistry, University of Barcelona, Spain). Homogenised soil samples were extracted either by acetic acid or aqua regia as follows: acetic acid extraction –1 g of soil added to 40 ml 0.11 M acetic acid in a 75 ml stoppered tube, pH adjusted to 2.85, mix for 16 h. The mixture was centrifuged and the aqueous phase filtered (0.22 μm filter) to provide 40 ml extract. Aqua regia extraction – 0.25 g of soil was mixed with 9 ml aqua regia in pressure resistant vessels and allowed to predigest overnight. Samples were then heated to 200 °C over 4 min then maintained at this temperature for 6 min (max. pressure 180 psi). The vessels were cooled to ambient and the whole solution filtered (0.22 μm filter), then made up to 100 ml with addition of 1 ppm Au for mercury stabilisation. Samples were stored at 4 °C prior to use. Mine water samples were filtered (0.2 μm filter) then diluted 1:10 or 1:100 in aqua regia. Samples were analysed by ICP-MS and ICP-OES (high metal concentrations) according to EPA standard methods.

2.7 PURE project samples and standard methods

Eighty-two soil samples (denoted ‘PURE’, see Acknowledgments) were supplied in two sets (set 1 = 25 samples; set 2 = 57 samples). Metal analyte concentrations were obtained independently using EPA method #6020 A/98 (ICP-MS). The samples were supplied air dried and sieved to obtain the <2 mm fraction for analysis. All samples were stored in airtight containers at 4 °C. A natural matrix soil CRM (CRM023-050, Resource Technology Corporation [RTC], Laramie, WY, USA) was used for quality control purposes and to evaluate precision and accuracy of the on site analyte extraction procedure.

2.8 Data analysis

The relative standard deviation (RSD), expressed as a percentage, was used as a measure of the achieved precision, and is defined as 100 s/x, where s = standard deviation and x = arithmetic mean (Miller & Miller, 2000). This is routinely used to evaluate analytical methods. The results obtained from the certified reference materials, expressed as a percentage of the certified values, were used as a measure of the achieved accuracy. These are commonly referred to as recovery rates. This shows the efficiency of the extraction procedure in bringing into solution the analytes of interest, and an indicate any gross errors and matrix effects. Once a recovery rate has been established, this can then be used to calculate the total concentration of the analytes in the sample. To validate the *in situ* method and identify any systematic errors, regression analysis was undertaken. When the sample yields an identical result with both methods, the regression line will have a zero intercept and a slope and correlation coefficient of one. However, this is rare, as random error ensure that the two methods will not give results in exact agreement for all the samples.

3 Results and Discussion

3.1 DPASV characterization

Following optimization of experimental protocol and carbon ink selection (Cooper, 1994), analytical performance of the field-based DPASV method was evaluated. Quantifiable stripping peaks were obtained for all three analytes (Figure 2). The broader and

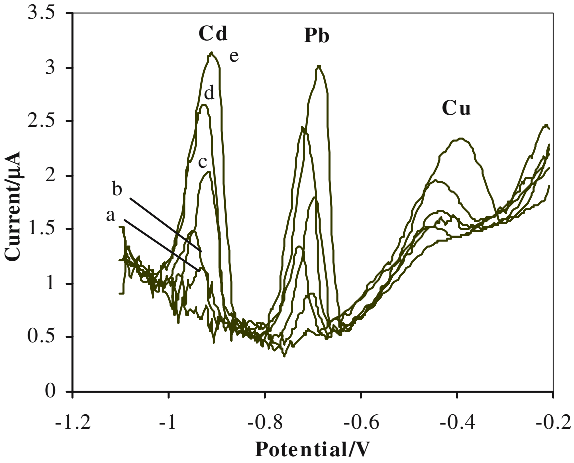


Figure 2 Voltammograms of Cd, Pb, and Cu in 100 mmol l^{-1} KCl, 1% v/v HNO$_3$; t_{dep}, −165 s; E_{dep}, −1.1 V; E_{scan}, −1.1 V ⇒ −0.2 V at 20 mV s^{-1}; (a) 10 μg l^{-1}; (b) 50 μg l^{-1}; (c) 100 μg l^{-1}; (d) 150 μg l^{-1}; (e) 200 μg l^{-1}.

less well-defined Cu peak was considered due to the proximity of the Cu and Hg film oxidation potentials, irreversibility of the Cu^{2+} reduction (Bradshaw & Scollary, 1997; Kadara et al., 2003) and the possible formation of insoluble Hg compounds, such as calomel, on the electrode surface due to the presence of Hg and chloride ions in the test solution (Jagner, Sahlin, & Renman, 1995; Nolan & Kounaves, 1999, 2000; Zakharchuk, Saraeva, Borisova, & Brainina, 1999). This is reflected in the poorer correlation coefficient of 0.9970 achieved for Cu, as discussed below.

Calibration plots were linear up to 150 μg l^{-1} with correlation coefficients (r^2) of 0.9967, 0.9981 and 0.9833 for Cd, Pb and Cu respectively. Polynomial relationships were evident up to 200 μg l^{-1}, with r^2 values of 0.9964 for Cd, 0.9987 for Pb and 0.9970 for Cu ($n = 5$). Precision was obtained *via* 10 replicates of 50 μg l^{-1} test solution, yielding relative standard deviations (RSDs) of 4.5%, 3.8% and 6.4% for Cd, Pb and Cu respectively. The limit of detection, calculated as 3 × standard deviation of the blank measurement, gave values of 9.1, 1.4 and 32.6 μg l^{-1} for Cd, Pb and Cu respectively. These detection limits are well below the most stringent residential use soil guideline values (SGVs) given in CLEA UK of 1–8 mg kg^{-1} for Cd, 450 mg kg^{-1} for Pb and the Dutch target level of 190 mg kg^{-1} for Cu. The SGVs are based on total concentrations, and the ASV technique measures the soluble free ion. However, under most conditions, the predominant soluble species in soils is the free ion M^{2+}, and the extraction method used would extract all but the most resistant silicate-bound fractions. In terms of compliance, laboratory testing would be obligatory. Stringent EQS and UK Drinking Water Standards can be met by increasing the depositioning time of the analysis. This increases the amount of an analyte being reduced at the electrode surface and hence an increase in the response is seen.

3.2 Field-based soil extraction method

CRM023-050 was extracted with 10 replicates and DPASV performed in triplicate on each extract. Analyte recoveries were calculated according to the formula in the footnote of Table II. Extraction by manual shake, followed by DPASV analysis resulted in ~50% recovery of the analytes. Variation in analyte recovery was expressed as relative standard deviation (RSD), with values of 9%–14%, presumably as a consequence of the short extraction time (3 min) and simplicity of the combined extraction-analysis procedure. In an attempt to improve analyte recovery, whilst maintaining simplicity and speed, the use of ultrasonication, as an alternative to manual shaking, was investigated. Ultrasonic extraction has often been employed to speed up laboratory-based extraction methods and is easily adopted for on-site analysis by utilising commercially available, portable battery-operated ultrasonic probes (Marin, Lopez-Gonzalvez, & Barbas, 2001; Perez-Cid, Lavilla, & Bendicho, 1998; Williams & D'Silva, 1994). Sonication increased recovery values (Table II) to 64.1%, 51.7% and 57.3% for Cd, Pb and Cu respectively with a decrease in RSD to 4%–8%.

The recovery values obtained are a summation of the efficiency of analyte removal from the soil extract coupled to the effects of soil matrix components on the subsequent DPASV analysis (Al-Merey, Al-Masri, & Bozou, 2002). The relationship between analyte response and analyte concentrations may be influenced by complexation or adsorption of the metals by other molecules present in the sample matrix, especially those of high organic content (Cuadros-Rodriguez, Gamiz-Gracia, Almansa-Lopez, & Bosque-Sendra, 2001). Surfactants, humic acids and proteins may adsorb at the electrode surface either before or during deposition. In most cases, this results in reduced peak currents due to reduction of effective electrode area (electrode fouling) or hindered diffusion of the metals to the mercury surface. There may also be an increase in metal oxidation potential leading to a shift in stripping peak potentials to more positive values (Brainina et al., 2001; Wang, 1994a).

Table II Recoveries and RSD of on site extraction and analysis using soil CRM (dry soil mg kg^{-1})

Analyte	Mean ASV Value	RSD (%)	Certified Value	Recovery (%)[a]
Shake				
Cd	6.05 ± 0.98	11.7	11.7	51.7
Pb	12.89 ± 0.92	9.8	25.6	50.4
Cu	9.65 ± 1.20	14.0	18.8	51.3
Ultrasonication				
Cd	7.77 ± 0.46	6.7	11.7	64.1
Pb	13.23 ± 0.39	4.8	25.6	51.7
Cu	10.77 ± 0.75	8.0	18.8	57.3

[a] Recovery = 100% × (certified value/mean value); ($n = 10$).

Matrix effects were investigated by analysing a number of PURE soil samples and CRM023-050. Following extraction by the on site method, extracts were analysed with and without a single-point standard addition of 50 μg kg^{-1} metal analyte. Compared to the control DPASV assays performed on spiked buffer solutions, the stripping response of the standard addition decreased by 6%–23% for Cd, 5%–26% for Pb and 11%–25% for Cu (Table III). Such values concur with ICP-MS analysis of the soil extracts, in which decreases of 5%–15% were noted for the metals, indicating that the extraction method has the greater effect on analyte recovery values (35%–40% decrease in metal concentration value) compared to matrix effects on the electrochemical detection step.

The observed peak reductions were considered to be due to electrode adsorption processes (fouling) rather than metal complexation, because of the strongly acidic assay conditions used which do not favour complexation (Frenzel, 1993). This is also suggested by examination of the resulting voltammograms in which no significant peak distortion or overlap was evident (Figure 3). The relatively minor changes in the peak shape and potential (small changes in potential being primarily concentration dependent) indicate that the main matrix effect is probably due to surface-active compounds at the mercury film-plated carbon electrode which hinder the transport of metals to the surface during depositioning and thus change the magnitude of the peak current (Frenzel, 1993; Wang & Luo, 1984). The variation in the extent of signal decrease can be related to differences in soil type including physicochemical properties; metal–soil complexation and the amount/type of interfering components present in the individual samples.

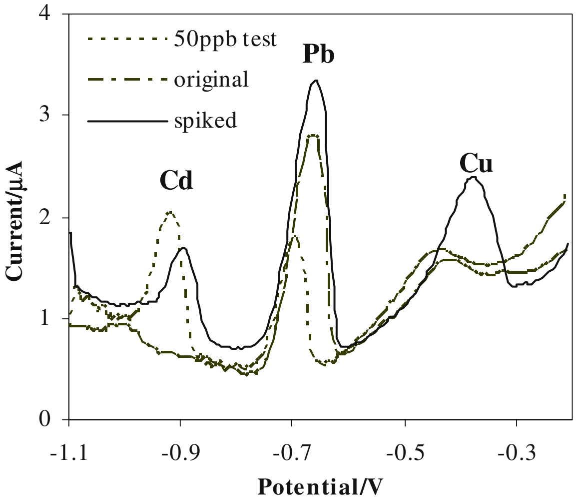


Figure 3 Stripping voltammograms of test solution and soil sample spiked (50 μg l^{-1}) and non-spiked. All experimental conditions as per Figure 2.

When site histories and initial site assessments indicate high organic matter, a single-point standard addition could be used to evaluate the impact of the soil matrix on the stripping response thereby reducing false negative results. A number of samples from the study area would also be sent to a centralised laboratory for validation testing, to mitigate the risk of false negatives being recorded. Alternatively, the more time-consuming multiple standard addition method, widely used in laboratory-based environmental matrix studies, may be employed. However, the

Table III Percentage of signal decrease in soil extracts following standard addition

	CRM	11	15	17
Cd				
Original extract value (μg kg^{-1})	80.6 ± 5.1	0	0	24.8 ± 4.9
Original + spike (50 μg l^{-1}) (μg kg^{-1})	122.7 ± 2.7	42.0 ± 8.1	38.6 ± 2.8	65.2 ± 3.2
Spike signal decrease %	5.98	15.9	22.9	12.8
Pb				
Original extract value (μg kg^{-1})	137.1 ± 9.5	187.8 ± 16.5	83.0 ± 5.2	156.5 ± 15.1
Original + spike (50 μg l^{-1}) (μg kg^{-1})	190.1 ± 9.1	182.3 ± 10.2	98.7 ± 7.6	178.7 ± 16.5
Spike signal decrease %	13.7	23.4	25.8	13.5
Cu				
Original extract value (μg kg^{-1})	111.6 ± 7.3	125.6 ± 5.5	68.2 ± 5.6	87.7 ± 24.1
Original + spike (50 μg l^{-1}) (μg kg^{-1})	122.1 ± 7.9	148.7 ± 4.1	105.4 ± 6.7	112.7 ± 17.5
Spike signal decrease %	24.5	15.3	10.9	18.1

Table IV Key analytical data drawn from the on site ASV assay and standard method results

	Cadmium[a]	Lead	Copper
Linear equation	$0.4951x + 0.0159$	$0.5431x + 1.7527$	$0.6298x - 1.1706$
Mean recoveries %	51.0	58.8	59.2
SD	10.8	8.3	10.2
RSD	21.9	14.2	17.2
RSD[b]			
<5%	10	41	34
5%–10%	10	30	30
10%–20%	1	11	13
>20%	3	0	5
Accuracy[c]			
±10%	9	36	32
±10%–20%	6	31	30
>±20%	9	15	20

Data is based on the data set of 82 samples. 58 of the samples contained cadmium levels below the limit of quantification of the ASV procedure.

[a] 58 of the samples supplied either had no Cd or Cd levels or were below the ASV limit of detection.

[b] Soil extracts measured in triplicate using new SPE for each measurement.

[c] Calculated as: 100% × ([ASV value − standard value]/standard value). Standard values were calculated using line of best fit data.

direct calibration method is preferable for reasons of assay and data treatment simplicity, reduced operator input, reduced measurement time and fewer assay reagents (Cuadros-Rodriguez et al., 2001). The field-based DPASV procedure was able to distinguish between spiked and unspiked samples at low analyte concentrations (50 μg kg^{-1}), suggesting that the method has potential for rapid site screening purposes against legal threshold values, such as CLEA UK SGVs as discussed above. Due to these specific limitations, and the requirement to simplify the analytical procedure for practical on site implementation, semi-quantitative data only is achievable.

Whilst analyte recoveries would be enhanced by the usage of more aggressive extraction procedures, such as use of stronger acids, addition of other oxidising agents (e.g., H_2O_2) and heating, interviews with site analysts have raised issues of operator health and safety and assay simplicity in the industry up-take of any field-based analytical method. Overall, the analyte recoveries of 50% were deemed useful in the context of rapid site characterisation by practicing site remediation consultants and other technical experts consulted on this issue (personal communication with members of the SENSPOL community, European Commission Thematic Network, 2000–2003; http://www.cranfield.ac.uk/biotech/senspol/).

3.3 Analysis of PURE soil samples

The combined extraction/DPASV procedure was examined using the PURE panel of 82 samples containing various soil types and analyte concentrations. The soil samples were alluvial sediments, varying in colour (from light tan to dark brown). The samples were supplied air dried and sieved. Key analytical data are presented in Table IV. The acid shake/DPASV procedure correlated with EPA method #3051A extraction and EPA method #6020 ICP, as evidenced by regression coefficient values of 0.9782, 0.9728 and 0.9869 for Pb, Cd and Cu respectively, the statistical significance of this correlation being confirmed using a two-sided *t*-test. The standard EPA method data was supplied by Snamprogetti Spa, Italy (see Acknowledgments). Mean recoveries for Cd, Pb and Cu were 51.0%, 58.8% and 59.2% respectively (RSD, 14.2%–21.9%). RSD values of <20% were recorded for all Pb samples, 21/24 Cd samples in which a Cd response was observed by ASV and 77/82 Cu samples ($n = 3$).

Accuracy was calculated by adjusting the EPA standard method values to reflect the recovery values of the on site ASV assay. This was calculated according to the line of best-fit equations in Table IV and then calculating the accuracy between the ASV and adjusted standard values according to the formula shown in the footnote of the Table. A total of 67/82

Table V Inter-assay comparison of key analytical data collected by on site ASV for sample sets 1 and 2

	Set 1	Set 2
Lead		
Mean recovery (%)	63.3	56.9
Correlation coefficient	0.9841	0.9711
Mean RSD (%) ANOVA	10.2	9.2
Copper		
Mean recovery (%)	63.9	57.1
Correlation coefficient	0.8824	0.9907
Mean RSD (%) ANOVA	15.1	28.0

Table VI Pb, Cd and Cu in soil/sediments extracted by aqua regia (dry soil mg kg^{-1})

Sample	683	684	685	686	687	688	689	690	691	692	721	722
Pb												
ICP	872	977	292	47	140	179	13	40	1,116	1,111	245	1,853
ASV$_{\text{lab}}$	972	1,072	286	46	120	157	6.9	33	646	775	255	1,998
Recovery$_{\text{lab}}$ (%)	112	110	98	97	85	88	53	82	58	70	104	107
RSD$_{\text{lab}}$ (%)	6.2	3.3	8.9	0.6	4.7	1.9	3.2	8.8	6.8	1.9	4.2	2.3
ASV$_{\text{field}}$	1,072	1,033	310	46	60	41	n	25	1,412	n	n	–
Recovery$_{\text{field}}$ (%)	23	106	106	98	43	23	–	63	127	–	–	–
Cu												
ICP	666	349	254	34	66	72	12	20	518	508	199	419
ASV$_{\text{lab}}$	440	328	158	18	51	56	12	17	518	387	206	327
Recovery$_{\text{lab}}$ (%)	66	94	62	54	77	77	100	84	100	76	103	97
RSD$_{\text{lab}}$ (%)	9.6	6.1	13.9	16.1	10.2	7	12.1	4.7	8.4	4	3.7	8.7
ASV$_{\text{field}}$	460	196	278	93	167	162	143	147	662	n	n	–
Recovery$_{\text{field}}$ (%)	69	56	109	>150	>150	>150	>150	>150	128	–	–	–
Cd												
ICP	4	<2	<2	<2	<2	<2	<2	<2	20	19	16	12
ASV$_{\text{lab}}$	<2	<2	<2	<2	<2	<2	<2	<2	10	12.1	10	12.3
Recovery$_{\text{lab}}$ (%)	<50	na	na	na	na	na	na	na	52	64	63	103
RSD$_{\text{lab}}$ (%)									7.7	6.3	11.5	6.1
ASV$_{\text{field}}$	<2	<2	<2	<2	<2	<2	<2	<2	n	n	n	N
Recovery$_{\text{field}}$ (%)	<50	na	na	na	na	na	na	na	–	–	–	–

RSD: $n = 3$; *n* not analysed; *na* analyte concentration below that of standard method, ASV repeatability data not generated: 683–691 soil; 692 sediment; 721/2 soil CRM.

ASV$_{field}$ field analysis; *ASV$_{lab}$* laboratory analysis; Recovery$_{\text{field}}$ = (ASV$_{\text{field}}$/ICP) × 100%: Recovery$_{\text{lab}}$ = (ASV$_{\text{lab}}$/ICP) × 100%.

Pb samples, 15/24 Cd samples and 62/82 Cu samples were within ±20% of the adjusted standard analytical values. An inter-assay comparison of the on site ASV assay mean recoveries, correlation coefficient values and mean coefficient of variation data (calculated by analysis of variation method – ANOVA) for the two sample sets are detailed in Table V for Pb and Cu. The lower precision and accuracy values for certain Cu measurements reflect the relatively imprecise nature of DPASV for this analyte for reasons previously described.

3.4 Sample analysis Aznalcollar samples

The combined field-based extraction/DPASV technique was tested within a European Commission supported workshop on a metals contaminated site in Aznalcollar, Spain. The method was also tested with samples from a water treatment plant for mine wastes at the same site. Table VI contains ASV data obtained on site (ASV$_{\text{field}}$) and in the laboratory (ASV$_{\text{lab}}$) against ICP-OES (ICP) data for samples extracted using the aqua regia extraction method. ASV$_{\text{lab}}$ and ASV$_{\text{field}}$ data for Pb exhibits a correlation to the values determined by ICP-OES, delineating those samples containing high and low (13–872 mg kg^{-1}) analyte concentrations. The ASV$_{\text{lab}}$ data for Cu varied from 54% to 103% of the values recorded by the

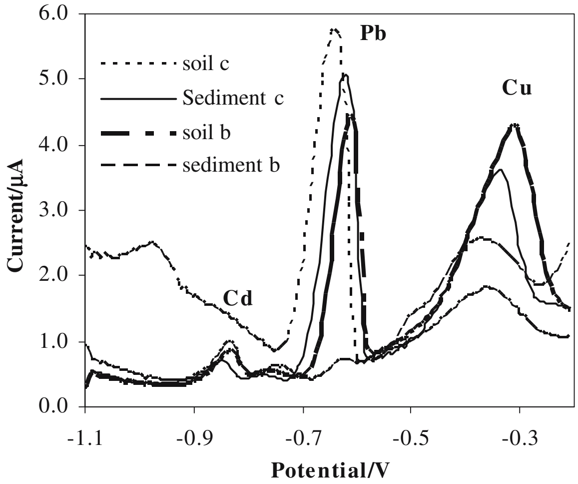


Figure 4 DPASV assay of Cd, Pb and Cu in a soil and sediment sample, extracted using either acetic acid (b) or aqua regia (c). All experimental parameters as per Figure 2.

Table VII Pb, Cd and Cu in soil/sediment extracted by acetic acid method (dry soil mg kg^{-1})

Sample	683	684	685	686	687	688	689	690	691	692	721
Pb											
ICP	119	59	6.0	2.0	1.2	7.0	<0.4	<0.4	109	14	2.4
ASV$_{\text{lab}}$	112	66	5.0	3.0	0.8	7.0	<0.4	<0.4	120	14	1.2
Recovery$_{\text{lab}}$ (%)	94	112	82	150	66	100	–	–	110	100	49
RSD$_{\text{lab}}$ (%)	3.5	4.0	13.7	5.0	3.2	3.4	na	na	1.6	6.0	22.2
Cu											
ICP	47	10	39	1.5	2.0	5.0	<0.4	<0.4	72	276	9.0
ASV$_{\text{lab}}$	46	9.0	38	0.97	0.88	3.4	<0.4	<0.4	68	234	8.4
Recovery$_{\text{lab}}$ (%)	97	90	96	65	44	68	–	–	95	85	95
RSD$_{\text{lab}}$ (%)	12.9	12.4	16.7	7.9	9.3	4.0	na	na	10.2	0.62	7.5
Cd											
ICP	2.37	0.64	1.04	<0.2	<0.2	<0.2	<0.2	<0.2	7.49	4.1	3.8
ASV$_{\text{lab}}$	1.69	0.42	0.99	<0.2	<0.2	<0.2	<0.2	<0.2	4.9	3.2	2.6
Recovery$_{\text{lab}}$ (%)	71	66	95	–	–	–	–	–	65	79	67
RSD$_{\text{lab}}$ (%)	3.1	2	8.3	na	na	Na	na	na	4.7	7.5	13

Recovery$_{\text{lab}}$ = (ASV$_{\text{lab}}$/ICP) × 100%; RSD: $n = 3$; 683–691 soil; 692 sediment; 721 soil CRM; na: analyte concentration below that of standard method, ASV repeatability data not generated.

standard method, but the ASV$_{\text{field}}$ data for Cu was higher than ICP-OES for most samples (>150% for 5/9 samples), again demonstrating the complicated and non-ideal determination of Cu by ASV. The ASV method correctly identified all those samples containing <2 mg kg^{-1} Cd by ICP-OES. A quantifiable stripping current was obtained for Cd in samples containing higher levels of this metal, as shown in Figure 4, with recoveries of 52%–103%. Analysis carried out in the laboratory (ASV$_{\text{lab}}$), following the field methodology, resulted in slightly improved RSD values for all analytes. ASV$_{\text{lab}}$ data is shown as a mean value, whereas ASV$_{\text{field}}$ values are from a single analysis, as would be the case in a rapid field-based screening method. The ASV$_{\text{field}}$ analysis precision (RSD) was generally <10% (23/28 measurements).

The samples extracted by the standard acetic acid method (Table VII) represent the ‘mobile’ analyte species recovered by this non-aggressive extraction method. The combined extraction/ASV assay yields data of a useful semi-quantitative nature for different samples and at lower analyte concentrations, when compared to the aqua regia/ICP-OES method. Recovery values for Cu and Cd were lower than for Pb. Soil water extract analysis proved inconclusive as these were below the limit of detection for the assay (extract ICP-MS values: Cd < 5, Pb/Cu < 10 μg l^{-1}). It may be possible to manipulate t_{dep} to improve assay detection limits. The samples containing high metal concentrations were from dump and workshop areas, whilst samples with low contaminant concentrations were from surrounding areas where either no history of mining was evident or where toxic floods had not

Table VIII Cd, Pb and Cu in water samples before (693, 694) and after (695, 696) treatment (mg l^{-1})

Sample	693	694	695	696
Pb				
ICP	0.89	0.74	<0.05	<0.05
ASV$_{\text{lab}}$	1.09	0.84	<0.05	<0.05
Recovery$_{\text{lab}}$ (%)	123	114	–	–
RSD(%)	9.3	8.3	–	–
ASV$_{\text{field}}$	1.11	1.02	0.02	0.02
Recovery$_{\text{field}}$ (%)	125	138	–	–
Cu				
ICP	0.18	0.18	<0.05	<0.05
ASV$_{\text{lab}}$	0.18	0.12	<0.05	<0.05
Recovery$_{\text{lab}}$ (%)	100	68	–	–
RSD(%)	18	15	–	–
ASV$_{\text{field}}$	–	1.78	0.05	0.05
Recovery$_{\text{field}}$ (%)	–	>150	–	–
Cd				
ICP	0.62	0.63	<0.05	<0.05
ASV$_{\text{lab}}$	0.74	0.89	<0.05	<0.05
Recovery$_{\text{lab}}$ (%)	119	141		
RSD(%)	8	3.9		
ASV$_{\text{field}}$	0.65	0.99	0.02	0.02
Recovery$_{\text{field}}$ (%)	105	>150	–	–

Recovery$_{\text{lab}}$ = (ASV/ICP) × 100%; RSD: $n = 3$.

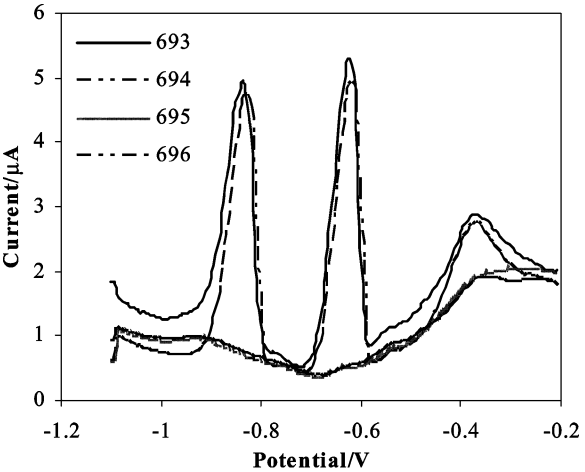


Figure 5 DPASV voltammograms for Cd, Pb and Cu in water treatment samples. All experimental parameters as per Figure 2.

previously occurred. This indicates the sensor device has potential for the mapping and characterization of pollution levels at the contaminated site and is capable of locating toxic ‘hotspots’.

Table VIII shows ICP and ASV data for water samples prior to and after entering the treatment plant at the contaminated site. Recoveries > 100% were recorded for Pb and Cd by ASV compared to ICP data and ASV was able to correctly identify the two samples containing no measurable Pb/Cd by ICP. Since all samples were prepared by simple acidification with aqua regia, the elevated recoveries may be attributed to matrix effects on the DPASV procedure. ASV_{lab} data for Cu correlated well with ICP data, again being able to identify the samples containing 0.18 mg l^{-1} Cu. Figure 5 illustrates the effectiveness of the assay in monitoring remediation processes, with well-defined stripping currents obtained from samples prior to treatment, but not post-treatment.

The Aznalcollar samples were also supplied in dried homogenised form, allowing evaluation of the combined field-based extraction + ASV determination method. Results are given in Table IX. ASV analysis yielded values of approximately 55% Cd, 58% Pb, and 48% Cu when compared to the aqua regia ICP-OES reference values. These mean recoveries are lower than those obtained for the same samples extracted using the pseudo-total method and analysed by ASV (Table VI), indicating that the recovery factor is dependent upon both extraction efficiency and matrix effects, factors routinely encountered using many alternative analytical techniques in soils analysis.

4 Conclusions

The results of ‘real’ sample analysis show that the on site ASV assay is capable of simultaneous analysis of Cd, Pb and, less precisely, Cu, in a range of soil types, extractant solutions and across a range of concentrations. Use of the direct calibration method provided a rapid means of quantification, without significant adverse matrix effects. This practical application of SPEs has shown to significantly reduce the complexity of the analysis, vital for field application. The on

Table IX Pb, Cd and Cu in soil/sediments extracted by field-based extraction method (mg kg^{-1})

Sample	683	684	685	686	687	688	689	690	691	692	721	722
Pb												
ICP	872	977	292	47	140	179	13	40	1,116	1,111	245	1,853
ASV_{Lab}	557	582	129	29	85	133	7	22	663	659	173	980
$\text{Recovery}_{\text{lab}}$ (%)	64	49	44	61	60	75	55	56	47	42	71	53
RSD (%)	6	5.5	6.3	8	4.1	2.4	8.9	3.2	2.1	3.4	1	3.7
Cu												
ICP	666	348	254	34	66	72	12	20	518	508	199	419
ASV_{Lab}	303	138	99	14	36	33	5.8	10	286	275	117	220
$\text{Recovery}_{\text{lab}}$ (%)ss	45	40	39	40	54	46	48	49	54	54	61	68
RSD (%)	4.4	6.2	9.2	11	28	9.4	13	19	4.3	4.7	5.8	9.4
Cd												
ICP	4	<2	<2	<2	<2	<2	<2	<2	20	19	16	12
ASV_{Lab}	2.3	nd	nd	nd	nd	nd	nd	nd	nd	nd	11.8	9.67
$\text{Recovery}_{\text{lab}}$ (%)	59								59	51	58	55
RSD (%)	6.5								4.6	2.6	2.6	8

site ASV assay is able to classify soils according to their heavy metals content, thereby reducing the number of samples requiring transfer to a centralised laboratory for further analysis. This reduction in more costly analytical treatment has clear economic benefits and hence is attractive to site owner, regulator and legislator alike. It also offers the potential for a greater number of samples to be tested without increase in budget, leading to more efficient and comprehensive environmental protection. In terms of practical implementation, on site instrumentation is already available (PalmSens). Screen printed electrodes are routinely printed for use in the medical industry i.e., blood glucose sensors, and companies such as DuPont can provide both proprietary inks, or inks and printing technology designed exclusively for customer needs. Further development of a range of on site soil extraction procedures, aimed at different metal fractions i.e., soluble bioavailable, recovered by water shake would expand the applicability of the on site sensor to a range of environmental studies, similar to laboratory sequential schemes. A user friendly field-based extraction ‘kit’ containing all necessary reagents and equipment would be a convenient way of providing data to meet the specific requirements of the end-user.

Site characterisation and monitoring are essential steps in land management. Demonstration of innovative field based techniques should increase awareness of the practical utility of these techniques to end-users, ultimately encouraging wider acceptance amongst environmental consultants and industry concerns alike.

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