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Miniaturization in voltammetry: Ultratrace element analysis and speciation with twenty-fold sample size reduction

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ABSTRACT

Voltammetric techniques have emerged as powerful methods for the determination and speciation of trace and ultratrace elements without any preconcentration in several research fields. Nevertheless, large sample volumes are typically required (10 mL), which strongly limits their application and/or the precision of the results. In this work, we report a 20-fold reduction in sample size for trace and ultratrace elemental determination and speciation by conventional voltammetric instrumentation, introducing the lowest amount of sample (0.5 mL) in which ultratrace detection has been performed up to now. This goal was achieved by a careful design of a new sample holder. Reliable, validated results were obtained for the determination of trace/ultratrace elements in rainwater (Cd, Co, Cu, Ni, Pb) and seawater (Cu). Moreover, copper speciation in seawater samples was consistently determined by competitive ligand equilibration–cathodic stripping voltammetry (CLE–CSV). The proposed apparatus showed several advantages: (1) 20-fold reduction in sample volume (the sample size is lowered from 120 to 6 mL for the CLE–CSV procedure); (2) decrease in analysis time due to the reduction in purging time up to 2.5 fold; (3) 20-fold drop in reagent consumption. Moreover, the analytical performances were not affected: similar detection capabilities, precision and accuracy were obtained. Application to sample of limited availability (e.g. porewaters, snow, rainwater, open ocean water, biological samples) and to the description of high resolution temporal trends may be easily foreseen.

1. Introduction

Voltammetric methods have experienced an unpaired growth in the field of elemental analysis in the last decades (see recent reviews covering different fields of voltammetric analysis, [1–7]). The possibility to exploit the richness of organometallic chemistry and to reach subnanomolar detection limits without sample pretreatment definitely boosted the development of a large number of methods based on adsorptive accumulation, especially coupled with catalytic enhancement [8,9]. The possibility to directly determine trace element speciation is another unique feature offered by these techniques through different detection schemes, the two most frequently used being pseudopolarography [10–12] and competitive ligand equilibration–cathodic stripping voltammetry (CLE–CSV, first example in [13] and a recent review including this procedure in [2]). Fast electronics and more efficient scanning modes should also be mentioned as they created the necessary conditions for the revitalization of voltammetric techniques (see [14]) for an historical perspective).

Nevertheless, sample throughput is the major factor limiting their extensive application.

Reducing analysis and operator time, retaining the detection capabilities of stripping voltammetric methods, is a first challenging task. It should be highlighted that extensive multielemental analysis may be difficultly achieved: the use of mixed ligands [15] or of sequential procedures [16] enabled the determination of up to six elements in the same sample aliquot but advancement in this direction may be difficultly foreseen. Accordingly, analysis and operator time might be reduced by lowering the pretreatment time (higher efficiency UV treatment unit [17], faster degassing methods), lowering the deposition times (introducing more and more efficient organic ligands) and making automated methods available [18].

Sample size is the second fundamental limitation in the use of voltammetric techniques. Standard procedures in ultratrace analysis use 10 mL aliquots for quantification, whereas the CLE–CSV speciation protocol requires the analysis of approximately 12 sample aliquots with increasing metal additions for an overall volume of not less than 120 mL. Accordingly, reducing sample size would assure the extension to limitedly available specimens, concurrently reducing reagent consumption and possibly analysis time, as is usually true for other analytical methods (e.g. micro and

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nano HPLC [19]). Sample size reduction in voltammetry has mostly been achieved by miniaturization and the development of dedicated electrodes (see [20] for a review of pre-1997 papers). Microfluidic devices featuring solid state microelectrodes have been developed in the last two decades, with dramatic reduction in sample requirements [21–23]. Nevertheless, application at the trace and ultratrace level is presently limited to 10, rarely 5, millilitre samples.

Aim of the present paper is to introduce a simple sample holder enabling the reliable determination of total concentration and speciation of metals at the ultratrace level in 500 microlitre aliquots. The new cell not just decreases sample volume requirements: advantages include ready adaptability to existing instrumentation with a minimum replacement of commercial hardware (only a new adapted stirrer is required), reduction in waste generation by requiring 20 times less reagents, and increase in sample throughput by reducing the purge time. The method was applied to both freshwaters and seawater to determine total concentrations and to perform speciation analysis of trace and ultratrace elements: comparison with reference materials or standard procedures, lead to a successful validation of the proposed apparatus.

2. Experimental section

2.1. Solution and standards

Ultrapure water produced by a Millipore MilliQ A10 system was used throughout (18.2 MΩ cm conductivity, 3 ppb TOC). Pure nitric and hydrochloric acids were produced by a quartz sub-boiling apparatus (Milestone DuoPur) from commercial nitric and hydrochloric acids. All plastic material used in this study was cleaned by successive soaking for one week in detergent, 30% HCl and 10%HCl with ultrapure water rinsing in between and prior to storage.

Standard solutions were prepared by dilution from 1000 mg/L standards from Fluka (cadmium, cobalt, copper, lead and nickel). A one molar buffer solution for copper analysis was prepared by dissolving the adequate amount of solid HEPES (2-[4-(2-hydroxyethyl)piperazin-1-yl]ethanesulfonic acid) and adding pure ammonia (Suprapur, Fluka) to a final pH of 8.0 (NBS scale). The one molar ammonia buffer was prepared by diluting adequate volumes of pure ammonia and purified hydrochloric acid. A ten millimolar salicylaldoxime (SA) solution was prepared dissolving purified SA in 0.1 M pure hydrochloric acid. Moreover, a 0.1 M dimethylglioxime (DMG) solution was prepared by dissolving purified dimethylglioxime sodium salt in ultrapure water.

Multistandard solutions for the calibration of Inductively Coupled Plasma–Mass Spectrometry (ICP–MS) were prepared by dilution of a multielement stock solution (10 mg/L from Merck, cat. no. 1.09498.001).

The reliability of copper analysis was checked by analysis of acidified consensus samples collected during the SAFe cruise [24], updated concentrations can be found in http://es.ucsc.edu/~kbruland/GeotracesSaFe/kwbGeotracesSaFe.html.

2.2. Sample collection and pretreatment

Clean procedures were adopted during sample collection and treatment. Rainwater was collected in Como (Northern Italy) during a rainfall event on 15/11/2013, from 9:10 a.m. to 11:40 a.m. at half an hour interval. The five samples were divided in two aliquots: a first 10 mL aliquot was acidified to pH 2 with quartz sub-distilled hydrochloric acid; the remaining sample aliquot (around 20 mL) was acidified with quartz sub-distilled nitric acid (final concentration 2%). Samples for the determination of total concentration by voltammetric techniques were UV irradiated for two hours in a home made 400 W apparatus [17].

Samples for analysis of organic copper speciation were collected at different depths (surface to −25 m) in Mahon Bay (Menorca Island, Balearic Islands) according to clean procedures and filtered online by 0.22 μm cartridges before storage in LDPE 250 mL bottles. Once on shore the bottles were immediately frozen and thawed the day before analysis.

2.3. Instrumentation

The measurements were performed on a 663 VA stand (Metrohm) controlled by a micro-Autolab potentiostat (Metrohm). The polarograph was equipped with a standard three electrode configuration: a mercury hanging drop electrode, a graphite rod as a counter electrode and a reference Ag/AgCl 3 M KCl reference electrode.

An iCAP Q ICP–MS from ThermoScientific was used for the determinations of Cd, Co, Cu, Ni and Pb in rainwater samples as a reference method.

2.4. Analytical procedures

All the voltammetric determinations were performed in a laminar flow hood. The differential pulse sweep was used for all the determinations: detailed instrumental parameters are listed in Table 1. A brief description of the procedures follows (see also [18]). Quantification in voltammetric determinations was performed by the standard addition method.

Anodic stripping voltammetry: cadmium, lead and copper. The 500 μL, UV digested, sample aliquot was transferred in the cell and concentrations quantified.

Cathodic stripping voltammetry: copper. 500 μL of UV digested sample were transferred to the cell, 5 μL of pure concentrated ammonia, 5 μL of HEPES buffer and 5 μL of SA solution (final concentration 25 μM) were added. The potential was held at −1.1 V during deposition and then switched to −0.1 V before the scan as this procedure ensures higher sensitivity [25].

Cathodic stripping voltammetry: nickel and cobalt. The 500 μL UV digested aliquot was transferred in the cell, 50 μL of ammonia buffer and 5 μL of DMG solution (final concentration 1 mM) were added (final pH around 9.5).

Metal titration (CLE–CSV), copper speciation. The method is based on competitive ligand equilibration with salicylaldoxime and CSV detection of the labile fraction [25]. 120 mL of sample were transferred to a preconditioned bottle: 1.2 mL of HEPES buffer and 60 μL of SA solution (final concentration 2 μM) were subsequently added. Ten mL aliquots were transferred to

Table 1
Instrumental parameters employed for the differential pulse sweep.

	Cu (AdSV)	Ni and Co (AdSV)	Cd, Pb and Cu (ASV)
Purging time (*s*)	120	150	150
Deposition potential (*V*)	−0.1 or −1.1*	−0.7	−1.15
Deposition time (*s*)	60	60	60
Equilibration time (*s*)	10	10	10
Start potential (*V*)	−0.1	−0.8	−1.15
End potential (*V*)	−0.6	−1.1	0.05
Pulse amplitude (*V*)	0.050	0.050	0.050
Pulse time (*s*)	0.04	0.04	0.04
Voltage step (*V*)	0.005	0.004	0.006
Voltage step time (*s*)	0.3	0.3	0.15
Sweep rate (*V/s*)	0.017	0.013	0.06

* −0.1 V was used for the speciation procedure whereas −1.1 V for the determination of copper total concentration.

polycarbonate 30 mL tubes and copper standard solution added to final concentrations of 0, 1, 2, 4, 8, 12, 16, 20, 25, 30, 35 nM. The samples were equilibrated overnight, typically 14 h. Signals were registered on 500 μL aliquots first: 500 μL from each tube were transferred to the small cell by a micropipette in order of increasing copper concentration and the signal read in triplicate. This procedure lasted 100 min on average. Subsequently, signal recording was performed using the standard 10 mL cell according to the same procedure, i.e. in order of increasing concentration, using the remaining 9.5 mL aliquots. The procedure employing the standard volume lasted 145 min on average.

Titration data were linearised according to the van den Berg–Ružic linearization [26,27]: non linear fitting [28] did not yield significantly different results. Errors in ligand concentration and logK' were calculated according to standard error propagation procedures [29].

Inductively Coupled Plasma–Mass Spectrometry (ICP–MS), nickel, cobalt, cadmium, lead and copper. Trace element concentrations in rainwater samples were determined by Inductively Coupled Plasma–Mass Spectrometry (ICP–MS) as a reference method, employing external calibration for quantification.

3. Results and discussion

3.1. Apparatus and procedures

A significant reduction in sample volume while retaining the standard three electrode configuration should overcome severe geometric constrains. Three electrodes plus the stirrer and the purging gas tube must be soaked into the sample volume: they all have a roughly cylindrical shape with diameters ranging from 1 mm (purging gas tube and counter electrode) to 2–3 mm (working and reference electrodes plus stirrer). Moreover, the mercury drop electrode needs a minimum sample volume to be operated: the Hg drop should be well submersed and the capillary free to swing when the drop is removed by the knocker.

Accordingly, the minimum sample volume was rationally determined as the minimum sample surface and height. The first one was determined by positioning the electrodes, the stirrer and the purging tube at the same height and measuring the minimum surface necessary to accommodate all of them. The minimum sample height was set to the lowest figure required to work the mercury drop electrode properly. As a result, the minimum required volume was precisely defined in terms of diameter (20 mm) and height (minimum 1.6 mm).

Several prototypes with different designs were manufactured from different materials according to these constrains: the geometry combining the simplest design and best usability was chosen. Our new low volume cell is a cylindrical quartz vessel (20 mm internal diameter, 6 mm height, 2 mm wall thickness) and it is designed as an insert to be placed inside the standard glass cell (see Fig. 1). Operationally, the sample holder was blown and subsequently lathed from quartz: a small handle was added to the cell rim to easily manipulate it. Quartz was chosen to ensure minimum memory effects and contamination.

The standard stirrer, although fitting into the small sample volume, did not provide an efficient stirring because of its slash cut end and its overall dimensions unnecessary for the small volume. Accordingly, a new, smaller agitating rod was lathed from polytetrafluoroethylene with a length of 55 mm, a diameter of 8 mm and a smaller, 1 mm diameter tip: a threaded inner hole in the upper part enabled the fastening to the rotor in the voltammetric stand. Furthermore, a polytetrafluoroethylene stand was lathed and placed at the bottom of the standard cell to keep the small

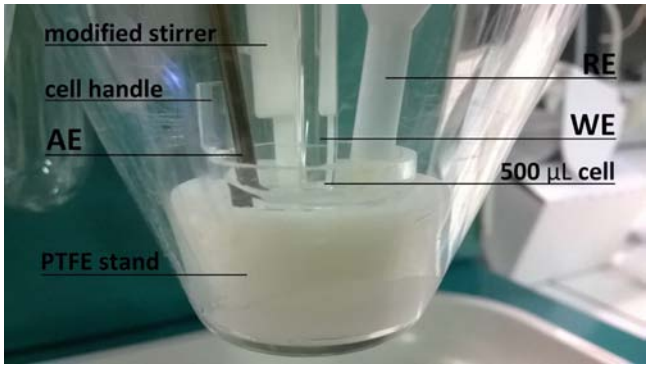

Fig. 1. Picture of the new hardware: the 500 μL cell, the modified stirrer and the polytetrafluoroethylene stand placed in the standard glass cell. Abbreviations: RE, reference electrode; WE, working electrode; AE, auxiliary electrode.

volume cell at the right height (see Fig. 1). The latter may be replaced by any adequate thickness of a plastic material.

A dramatic change in the purging procedure and time was an unexpected outcome of the reduction in sample volume. Preliminary experiments showed that the purging procedure could be extremely simplified: the purge tubing entering the sample was removed and nitrogen blown into the headspace from the lid covering the standard cell. The possibility to purge the headspace only is due to the high surface/volume ratio of the sample, being the sample height and diameter 1.6 mm and 20 mm, respectively. This feature ensures a fast diffusion of the gases to and from the sample volume: actually, early experiments in which the purge time was systematically changed demonstrated that 150 s are enough to achieve a satisfactory baseline with negligible changes observed for longer purge time. A two-fold reduction in the purge time was accordingly achieved with respect to the normal 300 s required by the 10 mL sample. For copper determinations, an even lower 120 s purge time could be used: a slightly higher baseline was registered although it did not interfere with the determinations.

The procedure to transfer the sample to and from the cell is the last modification introduced to the standard procedure. The removal of the sample was performed by a 100–1000 μL micropipette, ensuring a faster and more reliable procedure. Higher, random blanks were conversely obtained when the sample was poured out of the cell as usually done: actually, incomplete sample removal and/or contact of the specimen with the rims of the cell could lead to contamination.

3.2. Freshwater

The validation of the small cell for freshwater was performed on rainwater samples collected in Como, Italy: methods based on both anodic (Cd, Pb and Cu) and AdSV (Ni and Co) were tested. Detection capabilities as measured by limits of detection (LODs) were determined and compared to figures obtained by some of us in a recent paper with a similar apparatus and a standard 10 mL cell (a VA stand 663 in the present work vs. a 757 Computrace voltammeter in the previous work [18], both from Metrohm). As a result, no significant difference may be observed (Table 2): accordingly, detection capabilities were not deteriorated by the reduction in sample volume (see also the following section for seawater conditions).

Table 3 reports the trace element concentrations determined in the five rainwater samples: reference values obtained by ICP–MS are reported for comparison purposes. Standard deviations for voltammetric measurements are referred to triplicate independent measurements of sample aliquots, whereas uncertainty in ICP-MS

Table 2
Comparison between limits of detection determined in the present work and literature data. Note the different deposition times.

	Deposition time (s)	Limit of detection (ng/L)				
		Cd	Pb	Cu	Ni	Co
Present work 500 μL sample	60	30	35	64	8	12
Literature data 10 mL sample [18]	90	18	21	110	27	8.8

Table 3
Results of the analysis of the five rainwater samples by stripping voltammetry (anodic, ASV and adsorptive, AdSV) and Inductively Coupled Plasma–Mass Spectrometry (ICP–MS). Data are reported as mean ± one standard deviation in micrograms per liter, see text.

sample no.	Cd		Pb		Cu		Ni		Co	
	ASV	ICP–MS	ASV	ICP–MS	ASV	ICP–MS	AdSV	ICP–MS	AdSV	ICP–MS
1	< LOD	0.030 ± 0.003	0.3_9 ± 0.16	0.316 ± 0.002	3.77 ± 0.065	3.60 ± 0.058	7.2 ± 0.86	6.00 ± 0.053	0.036 ± 0.008	0.028 ± 0.002
2	< LOD	0.017 ± 0.001	0.25 ± 0.051	0.29 ± 0.016	1.77 ± 0.056	1.7 ± 0.10	1.30 ± 0.071	1.20 ± 0.011	0.027 ± 0.006	0.035 ± 0.003
3	< LOD	0.013 ± 0.001	0.28 ± 0.047	0.230 ± 0.002	0.98 ± 0.081	0.94 ± 0.013	0.51 ± 0.052*	0.411 ± 0.006	< LOD	0.008 ± 0.001
4	< LOD	0.013 ± 0.001	0.20 ± 0.015*	0.241 ± 0.001	1.35 ± 0.046	1.360 ± 0.007	1.4 ± 0.13	1.37 ± 0.010	< LOD	0.011 ± 0.001
5	< LOD	0.012 ± 0.001	0.27 ± 0.012	0.270 ± 0.003	1.35 ± 0.080*	1.17 ± 0.012	0.77 ± 0.036*	0.379 ± 0.004	< LOD	0.006 ± 0.001

* Values with statistically significant differences from ICP–MS data (two tailed *t* test, p=0.05).

data refers to triplicate readings of the same sample (i.e. it is an estimate of the short term repeatability).

No statistically significant difference was evidenced for all of the sample and analytes but in four cases (two tailed *t* test, p=0.05). Three of these differences were lower than 25% (or 0.1 μg/L in absolute figures), whereas the difference in nickel concentration in sample 5 was highly significant and possibly due to the contamination of the aliquot used for AdSV.

3.3. Seawater

The apparatus was initially validated for the determination of total copper concentration in a low level interlaboratory standard (SAFe D1, [24]). Three batches of the SAFe D1 standard were analyzed for copper: 2.5 ± 0.73 (n=9), 2.6 ± 0.49 (n=7) and 2.0 ± 0.15 (n=3) nanomol copper per kilogram were determined in 500 μL aliquots (mean ± standard deviation), with no significant difference from the consensus value of 2.27 ± 0.11 nmol/kg. Detection capabilities were also similar to the ones found in previous papers for 10 mL samples: a limit of detection of 0.13 nM was determined for copper (deposition time 60 s) against a 0.1 nM reported in the paper presenting the salicylaldoxime method [25], note that the latter refers to seawater, whereas the one determined here to ultrapure water.

Speciation analysis was validated by comparison with the standard procedure involving 10 mL aliquots using seawater samples from a surface-bottom vertical profile at the deepest point of Mahon bay (Minorca, Balearic Islands, Spain). Results are reported in Fig. 2 (see also Fig. S1). Both ligand concentrations and conditional stability constants K' did not show statistically significant differences if the random errors associated to the procedure are taken into account (see also Fig. S1). Furthermore, no systematic positive or negative difference may be appreciated from the data, showing that no artifact was introduced by the reduction in sample volume. In addition, precision did not show any degradation due to the 20-fold volume reduction: standard deviations associated to ligand concentrations and K' are comparable for the procedures using 10 and 0.5 mL aliquots and analogous to literature data for 10 mL aliquots (reported RSD% on real samples are around 10% for ligand concentrations and approx ± 0.2 for logK', see [29]). Along the profile, copper concentrations remained close (50–80%) to ligand concentrations, indicating a low buffering capacity to any episodic copper input to the bay.

4. Conclusions

A 20-fold reduction in sample requirement for trace and ultratrace elemental determination and speciation by conventional voltammetric instrumentation was successfully achieved. As a direct consequence, a 20-fold reduction in reagent consumption was accomplished and analysis time was strongly reduced because of the two-fold reduction in purge time. All of these features, i.e. minimal sample size, reduction in reagent use, decreased waste production and lower energy use compared to atomic spectrometric techniques, marks a step forward putting into practice the principles of green analytical chemistry [30]. The 0.5 mL volume introduced in this work is up to now the lowest amount of sample used for ultratrace analysis.

Moreover, the reduction in sample size did not affect the analytical performances in terms of detection capabilities, accuracy and precision.

The proposed apparatus opens new possibilities in voltammetric determination. It effectively reduces the gap in between standard voltammetric analysis requiring ten millilitre samples and specialised, non commercial setups which, up to date, were not demonstrated to fulfil ultratrace analysis requirements. Application to precious, costly or limitedly available specimen may be foreseen (e.g. biological and small volume environmental samples): understanding temporal (as shown here for rainwater) and/or spatial trends is an interesting possibility among others. As an example, the characterization of the complexing capacity of the dissolved natural organic matter (NOM) in porewater, would be experimentally within reach: the thermodynamic data of complexing species would allow modeling of trace metal mobility and bioavailability.

Further hardware development may be also foreseen. Automatization of the procedure for both total concentration and speciation analysis would be highly beneficial. The small volumes involved call for the use of recent analytical platforms, like lab on a chip (LoC) or lab on a valve (LoV) strategies.

On the other hand, further reduction of sample volume in a standard three electrode configuration may be difficultly achieved

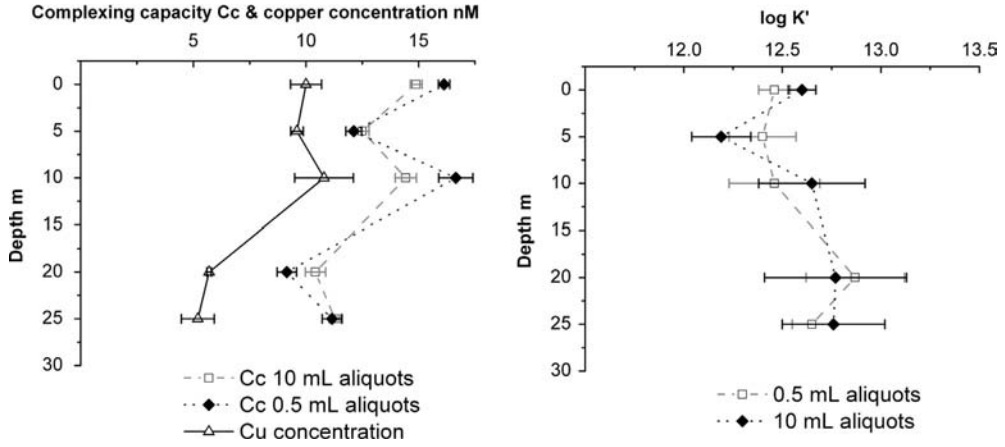

Fig. 2. Speciation analysis results: comparison between the proposed new method (0.5 mL aliquots) and the standard procedure (10 mL aliquots). Total copper concentration in the water column is also reported.

due to geometric limitations: miniaturization of the electrodes and possibly different working electrodes, i.e. solid state electrodes, should be pursued, although retaining the performances of standard mercury electrode is at present out of reach.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.04.024.

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