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Stripping voltammetry for field determination of traces of copper in soil extracts and natural waters

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Abstract

Field analysis is becoming increasingly popular, owing to the commercial availability of portable instruments, fast response and cost-effectiveness. Nevertheless, field analysis requires a careful planning. Voltammetry is particularly suitable for the field determination of trace elements thanks to its sensitivity, simplicity of operation and instrument portability. Therefore, in this work, Anodic Stripping Voltammetry (ASV) was applied to the field determination of Cu(II), as a pilot analyte, in natural water and in a soil extract, and the experiment organization was carefully detailed. Four solid electrodes were previously tested in the laboratory and their performances in terms of precision, linearity, trueness and overall ease of operation were discussed. The well-known Mercury Film Glassy Carbon Electrode (MF-GCE) was selected for field measurements because it yielded the most satisfactory performances. Anyway, the suggestions given in this paper can be useful for other electrodes and other analytes; in particular, a list of the items that should be brought to the site where analysis will be carried out was proposed in order to provide a general guide for the organization of field measurements by voltammetry.

Keywords: Voltammetry; field analysis; metal traces; water analysis; soil analysis

1. Introduction

Chemical analyses are essential in many fields, such as environment, food production, industry, forensic science and medicine, for decision making and quality control purposes. The availability of data in real time, at low costs but with a satisfactory reliability is very useful, as it enables one to organize rapid interventions in case of emergency, to extensively monitor the phenomena of interest, to choose further sampling points and reduce the number of samples requiring additional investigations in the laboratory. For this reason, much attention is devoted to the development of instruments and procedures for field analysis [1]. Some parameters are already routinely determined on site, or even in-situ: for instance multiparameter water probes allow the measurement of many physical-chemical properties, such as temperature, conductivity, pH, redox potential and dissolved oxygen level, to be performed directly in a water body. In

clinical analysis, bedside and personal devices for blood analysis are available, e.g. for the measurement of the glucose level.

Many instruments used in the analytical laboratory are commercially available in a portable version too: this is the case of UV-visible, near infrared (NIR), X-ray fluorescence or Raman spectrometers, and gas mass or gas-chromatographs [2-6]. Some field analysis techniques is also accepted in official methods of analysis [7,8].

Regarding the determination of metal ions, portable XRF devices are used for the analysis of solid samples, such as soils and rocks, whereas UV-visible spectroscopy is used to evaluate water quality [2,9]. These methods are not sensitive enough for the determination of elements at trace levels, while voltammetry is suitable for this purpose due to its high sensitivity, the applicability to a large number of analytes, low instrument purchase and operation costs [10-12]. Many procedures for voltammetric field analysis have been developed, thanks to the availability of a number of commercial portable potentiostats [13]; the technique of choice is usually stripping voltammetry, which encompasses an analyte enrichment step. Portable voltammetric analyzers can be connected to conventional solid electrodes modified with metal films, nanoparticles, polymers and/or ligands or other reagents[11,12]. In alternative, it is possible to use screen printed electrodes (SPE), again modified with reagents or materials able to preconcentrate the analyte(s) of interest [14,15]. SPEs are disposable, thanks to their low cost and to the possibility of mass production, so that electrode clean-up after the analysis and memory effects are avoided; the use of SPEs is expected to increase in the near future. Also single microelectrodes or microelectrode arrays have found application for field analysis [14,16]. A less common, but probably emerging approach is the use of micro-total-analysis-systems (m-TAS), i.e. lab-on-a-chip devices based on microfluidic [11,16]. Finally, in the last years remote sensing is increasing, thanks to the new wireless connection technologies [11,16].

Field voltammetric measurements for trace element determination have mainly addressed samples of environmental interest, typically waters [17], analyzed both on-site and in situ [18], but also soil and particulate matter [19,20]. However, most of the papers dealing with field analysis are focused on the description of the electrode structure and response, giving few information on the organization of the analysis itself, or simply demonstrate a proof-of-concept for metal ion detection. On the other hand, performing voltammetric measurements outside a laboratory requires a careful planning of the activities and of the devices, chemicals and accessories required.

This work reports a study aimed at the field determination of Cu(II), as a pilot analyte, in natural water and in a soil extract and carefully details the experiment organization. The measurements were carried out by Anodic Stripping Voltammetry (ASV) with a portable potentiostat. Four solid electrodes were preliminarily tested in the laboratory: a bare Carbon Paste Electrode (CPE), a Gold-modified CPE (Au-CPE), a Gold Nanoparticle-modified Glassy Carbon Electrode (AuNPs-GCE) and the well known Mercury Film Glassy Carbon Electrode (MF-GCE). The MF-GCE yielded the most satisfactory performances, so it was selected for

field measurements [21,22]. In addition, attention is given to the aspects that have to be taken into account when analyses are carried out outside laboratories, in order to provide a general guide for the organization of field measurements.

2. Materials and methods

2.1. Samples and sample pretreatment

The natural water samples analyzed in the laboratory ~~was~~ were collected by ARPA Piemonte, (the regional environmental protection agency) from Banna river, a small tributary of Po river, near Torino (44° 56' 54.3" N, 7° 43' 05.6" E) in June and July 2017. They were stored in 1 L dark glass bottles at 4 °C. Before the analysis the samples were filtered twice, first through a paper filter and then through a syringe membrane filter. Then they were added with hydrochloric acid, so as to reach a ~~final~~ concentration of 60 mM, at least one day before the analysis.

The water sample analyzed in field was collected from the same river using a polyethylene bottle, dipped into the water stream with the aid of a rope. The water was filtered and acidified as described above, and left standing 30 minutes before starting the measurements.

The soil sample analyzed in field was collected from an experimental urban garden in the city of Torino with the aid of a plastic trowel. After breaking the agglomerates, it was sieved through a 2mm sieve.

2.2. Apparatus and reagents

Standard Cu(II) solutions were prepared from concentrated stock solutions (Sigma Aldrich).

High purity water (HPW) produced with Millipore Milli-Q Plus system was used throughout. The reagents employed were of analytical grade. The GCE-based Working Electrodes (WEs) were prepared from a commercial Metrohm GCE (3 mm internal diameter).

Voltammetric analyses were performed with a portable PalmSens3 potentiostat equipped with a cell with three electrode configuration: a WE (see 2.3.1), a graphite rod as a counter electrode and an Ag/AgCl/KCl (3 M) as a reference electrode. The potentiostat was connected to an IKA-Topolino magnetic stirrer and interfaced to a laptop computer; the software PStTrace 4.6 was used to set up the operational conditions and to produce and record voltammograms. The computer was fed by its own battery during field analysis. The potentiostat weighs 430 g and has an internal battery. The device and the connecting cables are housed in a plastic case during transport or when not in use. A portable battery was used to feed the stirrer during field analyses.

Spectroscopic analyses of natural waters were performed with a Perkin Elmer Analyst 600 Graphite Furnace Atomic Absorption Spectrometer (GFAAS) equipped with an autosampler and Zeeman effect background

correction. The soil extract (see 2.3.4) was analyzed without dilution with a Perkin Elmer Optima 7000 inductively coupled plasma-optical emission spectrometer (ICP-OES).

2.3. Procedures

2.3.1. Preparation of WEs

Bare CPE. Bare CPEs were obtained by mixing graphite powder (nominal diameter < 20 μm , Aldrich) and paraffin oil in 70:30 weight ratio in a ceramic mortar. The paste was tightly packed into a home-made polypropylene support (internal diameter 4 mm) deriving from an Eppendorf syringe tip and a copper wire was introduced to ensure electrical contact with the potentiostat cable.

Au-CPE. Gold nanoparticles were synthesized according to a procedure described in ref. 243 [243]. An aqueous solution of tetrachloroauric acid was heated to boiling, then 5 ml of 1% sodium citrate were added. After a few seconds, the color of the solution turned to wine red, indicating the formation of Au nanoparticles. The solution was further heated for 30 minutes, then cooled to room temperature. Graphite powder (1 g) was added. Two procedures were compared to isolate the graphite-Au composite: vacuum filtration and freeze-drying; the latter was found to be more suitable (see 3.1.2). The functionalized graphite was mixed with paraffin oil and the paste was packed into the support as described for the bare CPE. Previous experiments by Scanning Electron Microscopy (SEM) showed that the Au particle size in the paste is 150-300 nm, suggesting that the nanoparticles partially coalesced during the preparation of the electrode.

AuNPs-GCE. The AuNPs were electrolytically deposited onto the GCE surface according to the a procedure previously developed by the authors [24,25]. Briefly, the GCE was polished with alumina powder, rinsed three times with ethanol and water, alternatively, and dried with a nitrogen stream. Then the electrode was dipped into a 100 mg/L $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ solution and connected to the potentiostat; a potential of -0.80 V was applied for 6 minutes to obtain the reduction of Au(III) and the formation of AuNPs, as confirmed by SEM analyses. The AuNPs-GCE was stored in 0.1 M NaOH. Before use, ten cyclic voltammetry scans from 0 to 1.50 V were performed in 0.5 M H_2SO_4 solution.

MF-GCE. The MF was electrolytically deposited onto the GCE surface [22]. The deposition can be carried out either ex-situ, i.e. before the analyses, or in-situ, whereby a mercury salt is added to the sample and the film is deposited together with the analyte(s). We chose the ex-situ approach in order to avoid the risk of contaminating the samples with impurities possibly present in the source of mercury and reduce reagent consumption. The GCE was polished as described for the AuNPs-GCE and dipped into a solution containing 2.3×10^{-3} M $\text{Hg}(\text{NO}_3)_2$ in 1×10^{-2} M KCl. The solution was purged for 300 s with nitrogen, then a potential of -1.0 V was applied for 20 minutes. After deposition the MF was cleaned by applying a potential of -0.15 V for 300 s, then a scan from -0.90 to -0.15 V was carried out (with the conditions described in section 2. 3.2) to verify the absence of impurities.

2.3.2. Voltammetric measurements

Voltammetric measurements were carried out by ASV. During the deposition step the test solutions were stirred and the potential was kept at -0.50 V for the first three electrodes and at -0.75 V for the MF-GCE. The deposition time ranged between 60 and 600 s, depending on the kind of WE and the concentration level (see 3.1). Then stirring was interrupted and, after 5 s of equilibration, a scan was performed in differential pulse (DP) mode with the following parameters: pulse potential 0.020 V, pulse time 0.015 μ s, step potential 0.004 V, scan rate 0.01 Vs^{-1} .

In laboratory experiments with standard solutions, 50 ml of 60 mM HCl were transferred into the voltammetric cell and a voltammogram of the blank was recorded. Then the required volumes of Cu(II) standard solution were added and the measurements were repeated.

In laboratory experiments with natural water, 50 ml of the pretreated sample (see 2.1) were transferred into the cell and the voltammogram of the sample was recorded. The measurements were repeated after adding successive aliquots of Cu(II) standard solution.

For the bare CPE and the Au-CPE, the electrode surface was renewed after each set of measurements carried out in the same cell, by discarding the outer layer of paste with the aid of a plastic piston. The freshly exposed paste was smoothed on a sheet of weighing paper. The performance of the AuNPs-GCE typically got worse after about 100 measurements: in this case the gold layer was dissolved by scanning the potential from by varying the potential from 0 V to 1.6 V in 6 M HCl whilst stirring the electrode and a new layer was deposited. The MF was wiped off and deposited again if defects were visually detected or when its response worsened. Typically, the MF-GCE could be used for three days before being renewed.

Before each measurement with the bare CPE, the Au-CPE and the AuNPs-GCE, a cleaning step of 0.50 V was applied for 60 s, to help removal of Cu(0), possibly left from the previous experiments, trapped in the paste or in the gold layer. Regarding the MF-GCE, after each stripping scan a potential 0.05 V was applied for 180 s, to oxidize residues of Cu possibly remaining in the film.

2.3.3. Field voltammetric analyses

Field analyses were planned in advance in the laboratory. Table 1 shows a list of the items required.

The day before field measurements the MF-GCE was prepared in the laboratory and its suitability was checked by analyzing a Cu(II) standard solution. Two cells were cleaned with nitric acid and rinsed with water. The cells and the electrodes were sealed in order to avoid contamination during transport. In alternative, the film can be deposited in the field, but a portable nitrogen cylinder would be necessary to purge the solution: attempts to prepare the MF without purging did not lead to satisfactory results.

Water analyses were carried out in a meadow close to the river, on a folding table placed so as to be as flat as possible. The measurements were carried out in duplicate, applying the conditions described in section

2.3.2, with a deposition time of 600 s. The concentration was quantified with the standard addition method. The deposition time was selected taking into account the concentration level found in the previous laboratory measurements; if no information on the sample is available, a preliminary experiment with increasing deposition times is necessary.

Regarding the soil, 20 g of sample were weighed, added with 50 ml of 1 M NH_4NO_3 , and shaken for 2 hours on a magnetic stirrer. The supernatant was filtered through paper filters three times. Then 2 ml were diluted to 10 ml with HCl so as to reach a conceivable final concentration of 60 mM. The voltammetric analysis was carried out in triplicate, applying the conditions described in section 2.3.2, with a deposition time of 300 s. The concentration was quantified with the standard addition method (two successive 10 $\mu\text{g/L}$ additions). Two cells were used, one for sample measurements and the other for electrode cleaning: this procedure enabled to limit contamination and speed up the analysis, since the sample solution was prepared while the electrode was cleaned in the other cell. Before analyzing the soil extract, a 10 $\mu\text{g/L}$ Cu(II) standard solution in the extractant (2 ml diluted to 10 ml) was analyzed to check the trueness and precision of the procedure in field conditions and in the absence of the soil matrix.

These measurements were carried out in winter. When the temperature was below zero, i.e. out of the range indicated by the manufacturer of the potentiostat (0-40 °C), noisy signals were recorded. For this reason the analysis was repeated in a nearby greenhouse, at 8 °C: the voltammetric analyzer worked regularly in these conditions.

The potential of reference electrodes depends on temperature. A temperature coefficient of -0.73 mV/°C with respect to 25°C, is reported for Ag/AgCl/KCl (3.5M), corresponding to the following equation: $E(T) = 205 - 0.73 \times (T - 25)$ [26]. We assumed that the same coefficient can be applied, at least as a first approximation, for Ag/AgCl/KCl (3 M), whose potential (vs NHE) is 210 mV at 25°C. Using the equation $E(T) = 210 - 0.73 \times (T - 25)$ we estimated that the potential of the reference electrode is 222.41 mV at 8°C. The temperature in the laboratory and near Banna River was about 22 °C, and the electrode potential can be estimated as 212.19 mV.

3. Results and discussion

3.1. Assessment and selection of WEs

There are plenty of methods in the scientific literature for the determination of Cu(II) by ASV, differing for the potential scan mode (DP or Square Wave) and especially for the nature of the WE (see e.g. references [11] and [12]). In this work the stripping scan was carried out by the well established and largely used DP mode; the values of the wave parameters (section 2.3.2) are those currently used in the authors' laboratory. The WEs tested were chosen on the basis of our previous experience or for their broad application in the literature; all four of them have a renewable surface, which permits to minimize memory effects, contamination and fouling. Moreover, the frequency of mechanical cleaning of the GCE is greatly

reduced when its surface is covered by a layer of modifier. Purging with nitrogen was found to be not necessary for Cu(II) determination, which makes field analysis easier. For the determination of other analytes, such as Pb or Cd, whose peak potentials are more heavily affected by oxygen reduction, small nitrogen cylinders can be used. The performance of each electrode was assessed considering three characteristics: within-cell and between-cell repeatability, evaluated from the relative standard deviation (% RSD); relationship between signal (peak height) and concentration, expressed by the equation of the regression line and the value of R^2 ; trueness (for the bare CPE and the MF-GCE), reported as the percentage relative error for the analysis of standard solution; ease of preparation and operation. The results are summarized in Table 2 and are discussed hereafter. Table 2 also reports the limits of detection (LoDs) for each WE, computed as three times the standard deviation of the blank. Figure 1 a-d shows the voltammograms obtained with each WE for increasing Cu(II) concentrations.

3.1.1. Bare carbon paste electrode

CPEs were developed in the 50s by Ralph Adams [27] and since then they have been extensively used for the determination of inorganic and organic analytes [28]. Their main advantages are the ease of preparation, the low cost of the starting materials, the wide range of potential and the versatility: CPE can be easily modified by mixing the proper modifier (metal nanoparticles, ligands, polymers, biological entities...) with the graphite powder. Another advantage is the possibility of renewing the surface just discarding the outer layer of paste: in the past, this electrode was considered as an alternative to the dropping mercury electrode for positive potentials. Nowadays CPEs are primarily used after modification, but in this work the bare form was tested as well, in order to gain insight into the performance of the graphite substrate and detect the effect of the modifier.

The comparison between the peak height with and without a deposition step confirms that Cu(0) is accumulated onto the electrode. The sensitivity in the concentration range 50-200 $\mu\text{g/L}$ increased about 20 times after 60 s of deposition. Experiments were carried out in two concentrations ranges: 50-200 and 5-20 $\mu\text{g/L}$. The % RSD for the peak height within the same cell ($n = 5$) was typically less than 5% in both ranges, which can be considered satisfactory. On the other hand, if the signal of different cells is compared, % RSD increased to about 25%, probably because the microscopic structure of the outer layer of the paste changes after renewal: SEM images (not shown) indicate that the paste is made of graphite flakes arranged in a random way, so the shape and the area of the surface in contact with the solution changes after extrusion, even if the paste is carefully smoothed. This result suggests the opportunity to carry out sample analysis with the standard addition method, so as to avoid to compare the signal measured in one cell with a calibration curve obtained in another cell; in alternative, samples might be quantified with external calibration without renewing the electrode surface: however, this procedure might be feasible only for the

analysis of samples with a simple, clean matrix, or for no more than one-two samples with more complex matrices, which would require frequent surface renewal.

The relationship between signal and concentration was examined both with and without deposition. An increase in response sensitivity was noticed with subsequent additions of aliquots of standard. This behavior was not clearly interpreted, since it would suggest the presence of a memory effect: however, no differences were observed when the duration of the cleaning step was doubled, and a scan in a blank solution after a set of experiments did not reveal the presence of stripped copper. The data in Table 2 show that the value of R^2 was higher for experiments with deposition and in the concentration range 50-200 $\mu\text{g/L}$ than in the range 5-20 $\mu\text{g/L}$; in addition linearity increased when the concentration range was narrowed. To assess trueness, three standard solutions at increasing concentration (30 – 70 – 140 $\mu\text{g/L}$) were analyzed. The relative error increased with decreasing concentrations. Attempts to fit the data with a polynomial curve and computing the concentration with the corresponding second order equation did not improve the trueness of the response.

The preparation of the bare CPE is simple, and can be carried out on site, and its surface is easily renewed. These characteristics, together with the cost effectiveness, are favorable for its use in field analysis. However, the results obtained suggest that the bare CPE would be suitable for this purpose only in the presence of relatively high concentrations, e.g. in the case of polluted waters. Longer deposition times were not applied to avoid the risk of a more extensive diffusion of the analyte within the paste, as reported in the literature [28].

In the next step of the work, a modifier was added to the CPE and its effect on the Cu(II) signal was assessed.

3.1.2. Gold-modified carbon paste electrode

Among the possible alternatives for the modification of CPE, gold particles were chosen [29]. Au-CPEs prepared with Au-graphite treated with vacuum filtration and freeze-drying were compared. The latter is time-consuming and requires a lyophilizer, which is not available in many laboratories. However, freeze-dried graphite provided a better performance; the results reported hereafter, and summarized in Table 2, are referred to this kind of graphite.

Experiments were performed in the range 100-300 $\mu\text{g/L}$, with a deposition time of 60 s. The within-cell repeatability ($n=5$) of the peak heights was below 5%; surprisingly, the % RSD for the signals of 100 $\mu\text{g/L}$ in three different cells was similar (4.5%). The relationship between signal and concentration was linear. The preparation of the Au-CPE is not simple, as it requires several steps, and obviously cannot be done in the field. Like the bare CPE, the renewal of the surface is simply obtained by extrusion.

Unexpectedly, the sensitivity and the LoD did not improve after modification with Au. This could imply that Cu is effectively deposited already onto the carbon paste and/or the modification procedure need to be

revised. It is possible that, adopting a different strategy for preparing Au-graphite, or using another modifier, the detection of Cu(II) would improve. Anyway, in this work it was decided to quit experiments with the Au-CPE (without assessing the trueness of the response), and test another substrate, namely glassy carbon, with two different modifiers.

3.1.3. Gold nanoparticle-modified glassy carbon electrode

Glassy carbon is the most popular substrate for modified electrodes, thanks to its chemical inertness, wide potential range, low background current, mechanical resistance, surface smoothness and relatively low cost (in comparison to noble metals).

The AuNPs-GCE tested as WE was previously developed by the authors and successfully tested for the determination of Hg(II) in several matrices [25,30]: a peak for Cu(II) had been detected during the investigation of potential interfering agents, so the electrode was expected to respond to this element too. Beyond the substrate, the AuNPs-GCE differs from the Au-CPE for three main features: i) the AuNPs are directly formed on the GCE surface by electrodeposition and do not need to be transferred after the preparation; ii) the Au particle size, estimated by SEM, is smaller, the average diameter being approximately 100 ± 25 nm; iii) Au is present only on the outer surface of the AuNPs-GCE, whereas it is distributed throughout the Au-CPE body.

Experiments were performed in two concentration ranges, namely 50-200 and 5-20 $\mu\text{g/L}$, with a deposition time of 60 s. In both cases, the voltammograms of the blank are characterized by a high background which makes it difficult to measure the peak height directly, especially at low analyte concentrations (see Figure 1c). The same problem had been encountered in the determination of Hg(II) [24], and it had been solved by blank subtraction. The same procedure was adopted here: well defined peaks were obtained. The Cu(II) peak is shifted to more positive potentials in comparison with the other WEs, suggesting the high affinity of Cu for Au nanoparticles. The within-cell repeatability ($n=5$) of the peak height was below 5% and between 5 and 16% in the ranges 50-200 and 5-20 $\mu\text{g/L}$ respectively. The between-cell repeatability was below 5% at 50 $\mu\text{g/L}$ level and decreased to 12% for 20 $\mu\text{g/L}$.

The linearity of the relationship between signal and concentration was excellent in the 50-200 $\mu\text{g/L}$ range, but poor between 5 and 20 $\mu\text{g/L}$, with a slight improvement if the concentration range was narrowed to 5-15 $\mu\text{g/L}$. The sensitivity of the response was higher than with the CPE and the Au-CPE, due to the electrocatalytical properties of AuNPs and their high surface area, confirming the previous findings on mercury determination [26]. Depositing AuNPs on the surface of the GCE by electrolysis was a more successful approach than mixing them with graphite. However, the LoD for the AuNPs-GCE are higher than for the CPE and the Au-CPE, because the variability of the blank is higher.

Probably, the performances of the AuNPs-GCE at low concentrations would improve if further experiments were carried out, e.g. increasing the deposition time. Anyway, additional experiments with the AuNPs-GCE

were given up, taking into account that the preparation of nanoparticles requires experienced personnel, a requirement not suitable for field methods. Therefore, another approach for the modification of the GCE was tested.

3.1.4. Mercury Film Glassy Carbon Electrode

The MF-GCE is a well-established WE and the preparation of the MF, even if not straightforward, is simpler than the deposition of AuNPs.

Longer deposition times were employed, in order to be able to determine low concentrations. The % RSD for the peak height within the same cell ($n = 5$) was below 5% in the concentration range 10-40 $\mu\text{g/L}$ (deposition time 180 s) and below 15% in the range 1-4 $\mu\text{g/L}$ (deposition time 600 s), with a few exceptions. The between-cell repeatability was similar (7.0 % for 1 $\mu\text{g/L}$) for voltammograms recorded on the same film, but dramatically dropped to 29 % using two different films (at 10 $\mu\text{g/L}$). This result is not unexpected, since the film is actually composed of a series of droplets and different arrangements can occur after different depositions. Therefore, when external calibration is used, it is advisable to quantify the concentration in a sample by relying on a calibration curve obtained on the same MF.

The relationship between signal and concentration was reasonably linear ($R^2 = 0.998$ and 0.993 in the ranges 10-40 and 1-4 $\mu\text{g/L}$ respectively). The trueness for the analysis of a 25 $\mu\text{g/L}$ Cu(II) standard solution was excellent (relative error 0.2%).

The peak heights recorded with the MF-GCE were lower than those measured with the AuNPs-GCE (e.g. at the 10 $\mu\text{g/L}$ level: 268 nA, with a deposition time of 180 s and 578 nA with a 60-s deposition time respectively). This might be due to a higher affinity of Cu for Au than for Hg and/or the higher surface area of AuNPs with respect to Hg droplets. The determination of 1 $\mu\text{g/L}$ of Cu(II) with the MF-GCE was feasible after applying a deposition time of 600 s. We hypothesize that the sensitivity of the response would increase if the electrode was rotated during the deposition step: in this work the solutions were stirred in order to have a simpler apparatus during field measurements.

The performances of the MF-GCE were deemed satisfactory: even if it is less sensitive than the AuNPs-GCE, it has a reasonable precision and accuracy, taking into account the low concentrations involved, and the preparation is relatively simple. One drawback is the need to use mercury, which gives rise to toxic wastes: therefore it is fundamental to collect the liquid wastes during the field analysis and transport them to the laboratory for a proper disposal. So the MF-GCE was selected for laboratory and field measurements of real samples. The literature reports several examples of the application of this electrode to field analysis (e.g. [21,31]), confirming its suitability for this purpose, even if the trend is toward the replacement of Hg with less toxic elements, such as Bi or Sb [11].

3.2. Analysis of natural water

3.2.1. Laboratory analysis

The Banna river water was firstly analyzed in the laboratory, in order to verify the behavior of the MF-GCE with the investigated matrix. The experimental conditions were the same as those adopted for standard solutions, with a deposition time of 600 s, due to the low concentrations expected. The concentrations in two samples, collected in two different months in 2017, were measured with the standard addition method. The results are summarized in Table 3. The linearity of the response for three successive additions of 1 µg/L of Cu to the water sample was good, especially for the sample collected in July. The trueness of the results was checked against a value determined by AAS, which was adopted as a reference value: the agreement between AAS and ASV was good for the June sample, but also the value obtained for July can be considered acceptable. ARPA Piemonte reports a concentration ≤ 5 µg/L for both samples, which is consistent with the results obtained in this study.

3.2.2. Field analysis

Before addressing a field analysis, it is important to plan it in the laboratory, taking into account the steps that will have to be carried out. The list of the items reported Table 1 can be a guide for other researchers for the organization of field measurements by voltammetry.

The analysis of Banna river water was carried out near the riverside. The deposition time was selected based on the concentrations found in the laboratory analyses. The increase of peak height with three successive additions of 1 µg/L of Cu(II) was reasonably linear. The concentration, measured with the standard addition method, was 1.70 µg/L, in fair agreement with the results found by GF-AAS (relative error -19 %). This level of error can be considered acceptable, considering that the field analysis is carried out in less controlled conditions. Nevertheless, the concentration found in the field analysis with the procedure developed in this study has to be interpreted with awareness of its limitation and is mainly useful for screening purposes. If a more accurate result is needed, the sample must be transferred to the laboratory; for instance, when the concentration found in a sample in field analysis is close to a threshold value, a further quantification in the laboratory is required.

3.3. Analysis of soil

The analysis of solid samples by voltammetry requires a previous dissolution step. In this study attention was focused on the concentration of Cu(II) soluble in a so called "soft extractant", which gives information on the metal mobility and availability and is used in the literature to predict the uptake by plants [3132]. The element concentrations extracted with these reagents are much lower than the total amounts, which can be determined only after mineralization with strong acid mixtures. Among the various single extraction

procedures reported in the literature, the extraction with NH_4NO_3 , which is standard national protocol in Germany, was selected [33], because it relies on a 2-hour extraction time, which is more compatible with field measurement than other methods requiring longer times.

Before analyzing the sample, the field determination of a $10.00 \mu\text{g/L}$ Cu(II) standard solution in the supporting electrolyte was carried out: as Table 3 shows, a good trueness and an acceptable precision were obtained. The corresponding voltammograms are displayed in Figure 2a. The concentration in the soil extract measured in field (Figure 2b) was in good agreement with the results obtained by ICP-OES, after correcting for dilution, but the % RSD was high, possibly because of the complexity of the matrix, which contains components extracted from the soil. Furthermore, it must be remembered that the concentration refers to a wet sample, since the soil cannot be dried in the time-scale of field analysis, which is more heterogeneous than dry ones. Therefore, the uncertainty in the result must be taken into account when interpreting the results, even if the average is close to the reference ICP-OES value. Overall the results obtained for the soil extract can be considered satisfactory, considering the relatively low concentrations involved and the complexity of the matrix.

4. Conclusions

Among the four tested electrodes, the MF-GCE turned out to be a suitable choice for the field determination of Cu(II) in natural waters and in soil extracts at few $\mu\text{g/L}$ level. In case of relatively higher concentrations, a bare CPE might be a suitable alternative, since the carbon paste is much cheaper than glassy carbon and the electrode is easily prepared.

The results of field analysis obtained with the proposed method can be used for screening purposes, and have to be interpreted taking into account their limitations.

The indications given in this paper can be useful for other electrodes and other analytes. In particular, a detailed list of the required equipment for the in field voltammetric measurements was reported with the intention to provide a useful tool to other researchers interested in this kind of analysis.

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Caption to figures

Figure 1. Voltammograms recorded at room temperature with (A) bare CPE, (B) Au-CPE, (C) AuNPs-GCE, and (D) MF-GCE, for increasing Cu(II) concentrations.

Figure 2. Voltammograms recorded in field (temperature 8 °C) for (A) 10 µg/L Cu(II) standard solution and (B) soil extract.

Table 1. Items necessary for field analysis

Aim	Item
General organization	Folding table Chairs Parasol (in case of hot weather) Portable battery Can for liquid wastes Tissue
Sampling	GPS navigator Bottles or spoon Items to reach the sampling point (e.g. rope)
Glassware and plasticware	Squeeze bottles with Milli-Q water Funnels
Chemicals	Reagents for the supporting electrolyte (or solution of the supporting electrolyte already prepared) and for the modification of the electrode In this study: HCl KCl Hg(NO ₃) ₂ Analyte standard solutions
Measurement	Potentiostat Cells (at least two) Electrodes Cell support with clamps Cables for connections Stirrer with stirrer bar Balance (for soil) Micropipets with tips

Table 2. Performances of the four investigated WEs.

Electrode	Signal repeatability	Signal-concentration relationship ¹	LoD and trueness
Bare CPE	% RSD ≤ 5% (within cell) 23% (between cells)	Without deposition, 50-200 µg/L: $y = 2.819 x - 109.68$ (0.206; 28.3) $R^2 = 0.9894$	LOD (without deposition): 15 µg/L Added: 140 µg/L Found: 145 µg/L (% RSD: 2.1) Relative error: 3.6%
		Without deposition, 50-150 µg/L: $y = 2.471 x - 80.64$ $R^2 = 0.9982$ (0.103; 11.15)	Added: 70 µg/L Found: 83 µg/L (% RSD: 3.6) Relative error: 18.6%
		Without deposition, 100-200 µg/L: $y = 3.111 x - 158.33$ (0.266; 41.43) $R^2 = 0.9927$	Added: 30 µg/L Found: 34 µg/L (% RSD: 1.8) Relative error: 13.3%
		After deposition (60 s), 50-200 µg/L: $y = 45.006 x - 1316.4$ (1.579; 216.2) $R^2 = 0.9975$	LOD (after 60 s deposition): 1.5 µg/L
		After deposition (60 s), 50-150 µg/L: $y = 42.309 x - 1091.7$ (0.593; 64.0) $R^2 = 0.9998$	
		After deposition (60 s), 100-200 µg/L: $y = 47.146 x - 1673.1$ (2.200; 342.0) $R^2 = 0.9978$	
		After deposition (60 s), 5-20 µg/L: $y = 28.062 x - 135.54$ (2.186; 29.93) $R^2 = 0.9880$	

¹In round brackets: uncertainties of slope and intercept

Table 2 (continued)

Electrode	Signal repeatability	Signal-concentration relationship ¹	LoD and trueness
Bare CPE		After deposition (60 s), 5-15 µg/L: $y = 24.984 x - 109.88$ (2.844; 30.72) $R^2 = 0.9872$ After deposition (60 s), 10-20 µg/L: $y = 31.757 x - 197.11$ (1.0667; 16.58) $R^2 = 0.9989$	
Au-CPE (freeze-dried graphite)	% RSD ≤ 5 % (within cell) 4.5% (between cells)	After deposition (60 s), 50-200 µg/L: $y = 21.344 x - 448.7$ (0.520; 112.3) $R^2 = 0.9994$	LOD (after 60 s deposition): 1.5 µg/L Trueness: not assessed
AuNPs-GCE	% RSD 50-200 µg/L: ≤ 5 % (within cell) 5-20 µg/L: 5-16 % (within cell) 50 µg/L: ≤ 5 % (between cells) 10 µg/L: 12% (between cells)	After deposition (60 s), 50-200 µg/L: $y = 55.121 x + 53.73$ (0.934; 127.9) $R^2 = 0.9994$ After deposition (60 s), 5-20 µg/L: $y = 62.056 x + 59.07$ (4.758; 65.15) $R^2 = 0.9884$ After deposition (60 s), 5-15 µg/L: $y = 54.782 x + 1.538$ (5.002; 54.023) $R^2 = 0.992$	LOD (after 60 s deposition): 10 µg/L Trueness: not assessed

¹In round brackets: uncertainties of slope and intercept

Table 2 (continued)

Electrode	Signal repeatability	Signal-concentration relationship ¹	LoD and trueness
MFE	% RSD 10-40 µg/L: ≤ 5 % (within cell) 1-4 µg/L: ≤ 15 % (within cell) 1 µg/L: 7 % (between cells, same film) 10 µg/L: 29% (between cells, different films)	After deposition (180 s), 10-40 µg/L: $y = 39.366 x - 109.8$ (1.109; 30,4) $R^2 = 0.9984$ After deposition (600 s), 1-4 µg/L: $y = 106.23 x - 4.725$ (6.33; 17.340) $R^2 = 0.9929$	LOD (after 180 s deposition): 1.2 µg/L (Laboratory analysis) Added: 25.00 µg/L Found: 25.04 µg/L (% RSD: 3.8) Relative error: 0.2% (Field analysis) Added: 10.00 µg/L Found: 9.51 µg/L (% RSD: 19.9) Relative error: -4.9% LOD (after 600 s deposition): 0.5 µg/L

¹In round brackets: uncertainties of slope and intercept

Table 3. Results obtained for water and soil analysis.

Sample	Expected	Found	% RSD	% Relative error	R^2 for standard addition plot
Banna river water, June 2017 sampling, (laboratory analysis)	1.46 µg/L	1.42 µg/L	8.3	- 2.8	0.9967
Banna river water, July 2017 sampling, (laboratory analysis)	1.86 µg/L	2.00 µg/L	15.3	7.0	0.9997
Banna river water, October 2017 (field analysis)	2.10 µg/L	1.70 µg/L	7.2	-19.0	0.9932
Standard solution prepared (field analysis)	10.00	9.51	19.9	-4.9	0.9981

Highlights

- Field analysis has several advantages, but requires a careful preliminary planning and organization.
- Anodic Stripping Voltammetry (ASV) was applied to the field determination of Cu(II), as a pilot analyte, in natural water and in a soil extract.
- Four solid electrodes were previously tested in the laboratory and the well-known Mercury Film Glassy Carbon Electrode (MF-GCE) was selected for field measurements because it yielded the most satisfactory performances.
- The experiment organization was carefully detailed in order to provide a general guide for the organization of field measurements by voltammetry

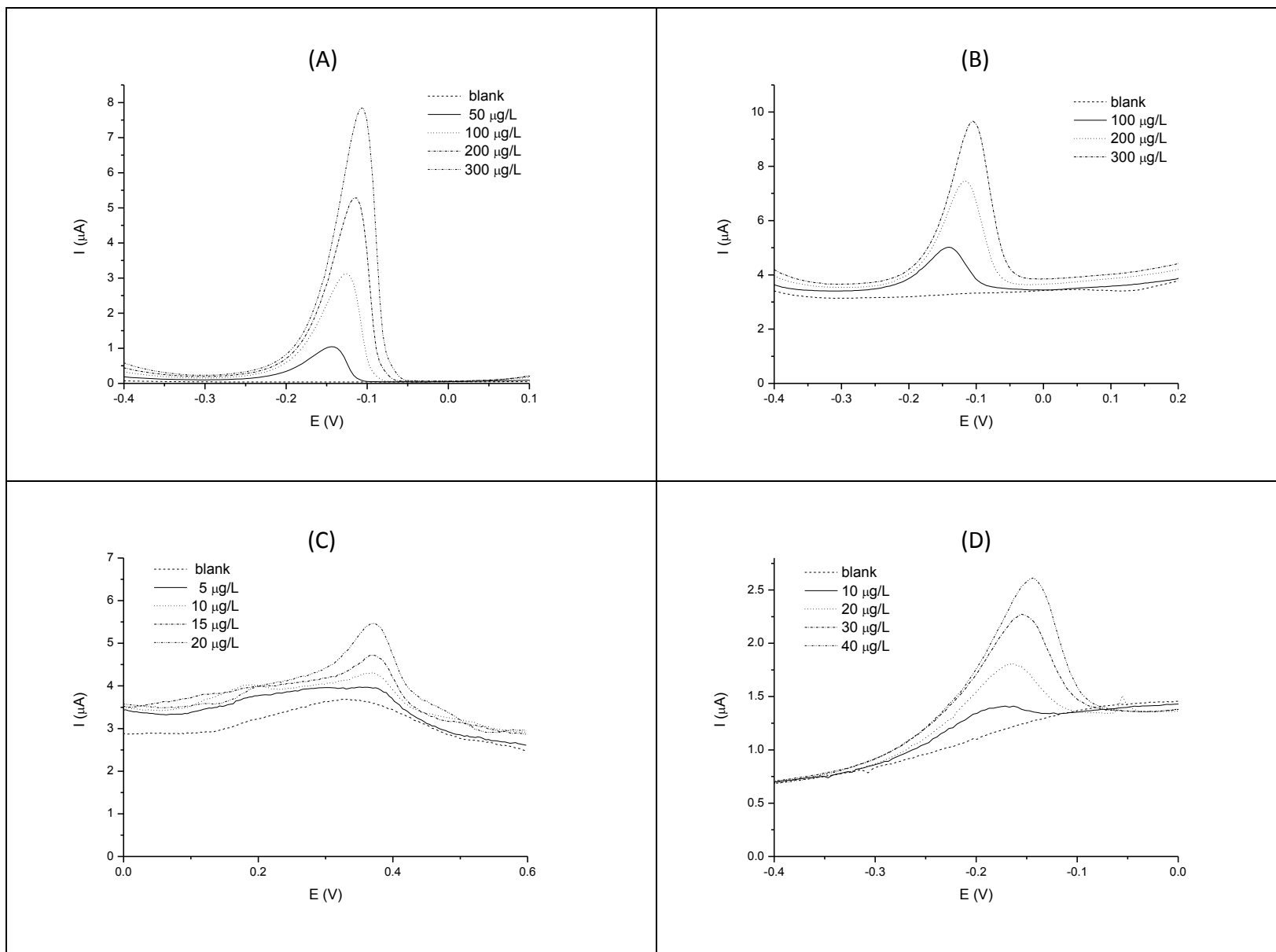


Figure 1

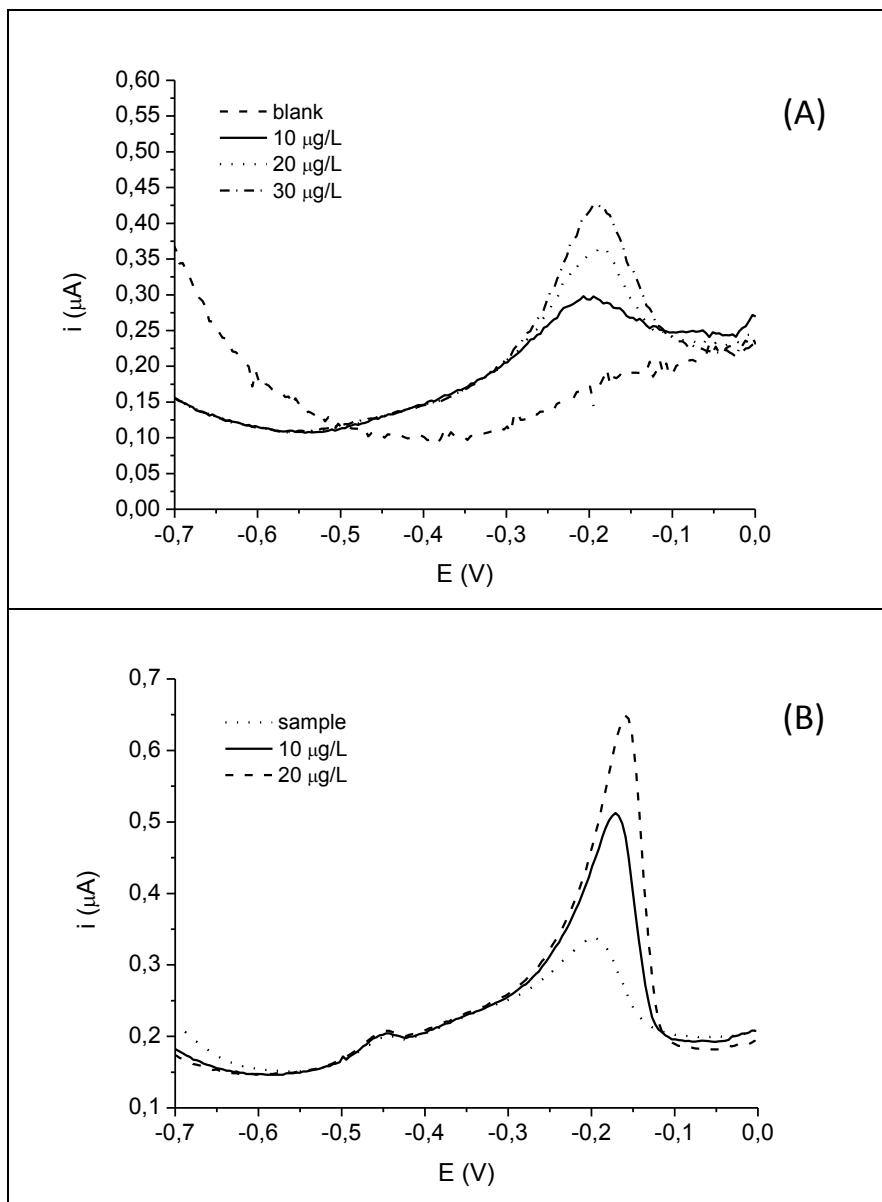


Figure 2