

VOLTAMMETRIC DETERMINATION OF METALS IN COPPER ALLOYS AT TRACE AND ULTRATRACE CONCENTRATIONSClinio LOCATELLI^{1,*} and Giancarlo TORSI²*Department of Chemistry "G. Ciamician", University of Bologna, via Selmi 2, 40126 Bologna, Italy; e-mail: ¹ clinio@ciam.unibo.it, ² torsi@ciam.unibo.it*

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Dedicated to Professor Sergio Roffia on the occasion of his retirement at the end of 2003, in recognition of his outstanding contribution to the development of experimental and theoretical supramolecular electrochemistry.

The present work describes the analytical procedures for the voltammetric determination of Cu, Pb, Cd, Zn, Fe, Mn, Co, Ni, Sn, Sb and Bi in copper alloys. The possibility of determining simultaneously metal concentrations in the case of interference of the voltammetric signals due to the peak overlapping is also highlighted and discussed. The analytical procedure was verified by the analysis of the standard reference materials: commercial bronze A NIST-SRM 1115, gunmetal BCS-CRM 207/2, high tensile brass BCS-CRM 390. Precision and accuracy, expressed as relative standard deviation and relative error, respectively, were in all cases lower than 6%. The limits of detection for each element were also reported.

Keywords: Copper alloys; Heavy metals; Trace analysis; Voltammetry; Atomic absorption spectroscopy; Electrochemistry.

The determination of metal species present in alloys are of great importance and regards several fields of interest.

Together with the problems linked to metallurgical industry¹⁻⁵, very important from the economic point of view, several other problems are present, like for example, the interaction that such kind of industry may have with the environment, evidently due to the industrial waste. For this reason, a careful and correct analytical procedure for the determination of metals present in alloy matrices is certainly necessary.

The possibility of determining simultaneously several metals at trace and ultratrace concentrations in real matrices has always stirred up great interest.

Spectroscopic^{6,7} and voltammetric⁸⁻¹⁰ measurements were perhaps the most important techniques for these goals. The voltammetric methods can be quite valid for the multicomponent metal analysis since a single poten-

tial scan, employing an appropriate supporting electrolyte, allows to obtain qualitative and quantitative information about the metal content in any real matrices with good sensitivity and selectivity.

Sensitivity has been improved by modern voltammetric techniques such as alternating and differential pulse voltammetry⁹ and by the introduction of new types of electrodes¹¹⁻¹³.

Good selectivity is obtained by employing particular techniques as the second harmonic alternating current voltammetry¹⁴ coupled¹⁵ or not¹⁶ with the standard addition method.

Anodic stripping voltammetry has been widely employed for the determination of metals in various organic and inorganic matrices¹⁰. Frequently, however, the sample preparation of complex matrices, as in the case of metal alloys^{10,17-21} is often very difficult, requiring various steps, that can cause errors in the analytical determination.

The present paper describes the analytical procedure for the simultaneous voltammetric determination of metals in copper alloys, especially highlighting the possibility of carrying out such a determination also in the case of interference of voltammetric signals.

EXPERIMENTAL

Apparatus

Voltammetry. Voltammetric curves were recorded with an Amel Model 433 multipolarograph, employing a conventional three-electrode cell: a hanging mercury drop electrode (HMDE) as a working electrode, an Ag/AgCl, saturated KCl reference electrode and platinum wire as reference and auxiliary electrode, respectively.

The Teflon voltammetric cell was rinsed every day with suprapure concentrated nitric acid in order to prevent any contamination. Standard additions were made with disposable plastic tips.

Keeping the temperature at 20.0 ± 0.5 °C, the solutions were deaerated with pure nitrogen for 5 min prior to the measurements, while a nitrogen blanket was maintained above the solution during the analysis. The solutions were deaerated after each standard addition for 1 min. In the electrolysis step the solutions were stirred with a magnetic stirrer.

Spectroscopy. Spectroscopic measurements were performed using a Perkin-Elmer Analyst 100 atomic absorption spectrometer, equipped with a deuterium background corrector, a premix, 10-cm titanium single-slot burner head, employing acetylene and air as fuel and oxidant, respectively (flame atomic absorption spectroscopy (FAAS)), a Perkin-Elmer HGA-800 graphite furnace (electrothermal atomic absorption spectroscopy (ETAAS)).

In all cases, single element Intensitron hollow-cathode lamps were employed. A mixture of palladium and magnesium nitrate was used as a matrix modifier in the ETAAS technique²².

The instrument settings used were those recommended by the Manufacturer²³.

Reagent and Reference Solution

Aqueous stock solutions 1000 mg l^{-1} (Merck, Germany) of copper, lead, cadmium, zinc, iron, manganese, cobalt, nickel, tin, antimony and bismuth were diluted with deionized water (Millipore, Milli-Q) for obtaining intermediate concentration solutions. Suprapure grade nitric, hydrochloric, perchloric acids, ammonium citrate and ammonia were used. Ammonia-ammonium chloride buffer solution was prepared by mixing an appropriate amount of hydrochloric acid and ammonia solutions.

Standard Reference Materials

The following standard reference materials were chosen for the analyses: commercial bronze A NIST-SRM 1115, gunmetal BCS-CRM 207/2 and high tensile brass BCS-CRM 390.

Sample Preparation and Experimental Conditions

The standard reference materials were mineralized in a different way according to the metals to determine.

Cu, Pb, Cd, Zn. Approximately 1.0 g, weighed accurately in a Pyrex digestion tube, connected with a Vigreux column to prevent and avoid any loss of the analytes, was dissolved in 10 ml of dilute (1:1) 69% (w/w) nitric acid. The tube was inserted into a cold home-made block digester, raising gradually the temperature up to $95 \text{ }^\circ\text{C}$ and keeping it for all the time of mineralization. After 15 min 10 ml, and after 30 min further 5 ml of concentrated nitric acid were added. Then, 5 ml of a dilute H_2O_2 (3:2; 30 volumes) were added, and, then, successively four times, every five minutes, 1 ml of the same solution. At the end, after cooling, 5 ml of 37% (w/w) hydrochloric acid was added, always maintaining the temperature at $95 \text{ }^\circ\text{C}$ for another 15 min. After cooling, the digest was diluted to 100 ml.

Voltammetric technique: DPASV. Experimental conditions: $E_d = -1.150$; $E_i = -1.150$; $E_f = +0.050$; $dE/dt = 10$; $f = 0.1$; $\Delta E = -0.050$; $v = 40$; $t_s = 8$; $t_d = 120$; $t_r = 15$; $t = 300$; $u = 600$. E_p : -0.160 ± 0.005 (Cu); -0.406 ± 0.010 (Pb); -0.623 ± 0.010 (Cd); -0.969 ± 0.005 (Zn).

Fe, Mn. Approximately 1.5–2.0 g, weighed accurately in a Pyrex digestion tube, connected with a Vigreux column to prevent and avoid any loss of the analytes, was dissolved in 8 ml of 37% (w/w) hydrochloric acid, and 10 ml of 69% (w/w) nitric acid was successively added. The tube, containing the standard materials and the acidic mixture, was inserted into a cold home-made block digester, the temperature of which was gradually raised. The solution was evaporated almost to dryness, and then, after cooling, the soluble salts were dissolved in 25.0 ml of ammonia-ammonium chloride buffer solution (pH 9.2).

Voltammetric technique: DPV. Experimental conditions: $E_i = -1.250$; $E_f = -1.850$; $dE/dt = 10$; $f = 0.1$; $\Delta E = -0.050$; $v = 40$; $t_s = 8$; $t = 300$. E_p : -1.506 ± 0.005 (Fe); -1.669 ± 0.010 (Mn).

Co, Ni. Approximately 0.5–1.0 g of sample, accurately weighed in a Pyrex digestion tube, connected with a Vigreux column, was dissolved in 5 ml of 37% (w/w) hydrochloric acid, and 8 ml of 69% (w/w) nitric acid was successively added. The tube, containing the sample and the acid mixture, was inserted into a cold home-made digester. After the initial reaction subsided, 7 ml of 60% (w/w) perchloric acid was added and the temperature gradually raised. The solution was evaporated until the sample was fully oxidized and fumes of perchloric acid appeared, allowing to fume for about 5 min. After cooling, the soluble salts were dissolved in about 100 ml of deionized water. The solution was filtered through a Whatman No. 541 filter paper and the filtrate diluted to 200 ml with deionized water (blank

tests demonstrated the concentrations of cobalt and nickel below detection limit of the voltammetric technique employed). Finally, 5 ml of the solution so obtained and 50 μl of the 0.1 M dimethylglyoxime in 96% ethanol (in order to obtain a final concentration equal to 1×10^{-4} mol l^{-1}) were diluted to 50 ml with 0.5 M ammonia–ammonium chloride buffer solution.

Voltammetric technique: DPAdSV. Experimental conditions: $E_a = -0.800$; $E_i = -0.800$; $E_f = -1.500$; $dE/dt = 15$; $f = 0.25$; $\Delta E = -0.050$; $v = 65$; $t_s = 8$; $t_a = 90$; $t_r = 30$; $t = 300$; $u = 800$. E_p : -1.135 ± 0.010 (Ni); -1.323 ± 0.010 (Co).

Sn, Sb, Bi. Approximately 0.5–1.0 g of sample, accurately weighed, connected with a Vigreux column, was dissolved in a Pyrex digestion tube by adding 7 ml of 37% (w/w) hydrochloric acid and, subsequently, 5 ml of 69% (w/w) nitric acid. After the initial reaction subsided, 10 ml of 60% (w/w) perchloric acid was added, and the solution was evaporated until the sample was fully oxidized and fumes of perchloric acid appeared. The solution so obtained was kept at the same temperature for about 30 min and evaporated to dryness. After cooling, the soluble salts were dissolved in 25 ml of 0.1 M ammonium citrate (pH 6.1).

Voltammetric technique: DPASV. Experimental conditions: $E_d = -1.150$; $E_i = -1.150$; $E_f = -0.100$; $dE/dt = 10$; $f = 0.1$; $\Delta E = -0.060$; $v = 40$; $t_s = 8$; $t_d = 150$; $t_r = 10$; $t = 300$; $u = 600$. E_p : -0.310 ± 0.010 (Bi); -0.662 ± 0.005 (Sn); -0.789 ± 0.005 (Sb).

RESULTS AND DISCUSSION

Prior to the analyses of standard reference materials, a preliminary study was carried out employing aqueous reference solution. The experimental conditions for the determination of the metals and the relevant experimental peak potentials are reported above.

Peak Overlapping Due to the Interference and Standard Addition Method

The reduction peak potentials of each metal, in the commonly used supporting electrolytes, are sometimes very close and thus simultaneous voltammetric determination could be hindered.

So, as expected, in the case of large excess of one component, an increasing overlapping of signals was observed in the measurement of the element present at lower concentration.

For this reason, the simultaneous voltammetric determination of each individual element in the presence of an interfering metal was studied in a wide range of concentration ratios in order either to evaluate the interference degree, or to establish the concentration ratio intervals within which no interferences were found.

Once the best experimental conditions were established, the analytical calibration function of each individual element was determined.

Successively, the element concentration ratios, within which each single metal was determined without interference, were investigated: to a fixed

concentration of the element of interest, standard amounts of an interfering element were added in such a way as to change their concentration ratios. The peak current values of the former element were then compared to those calculated, for the same concentrations, by using the analytical calibration function relevant to the individual element, and the relative errors were calculated.

The concentration ratios with a maximum experimental error of 5%, are the following (concentration expressed in $\mu\text{g g}^{-1}$):

Cu, Pb, Cd, Zn: $243:1 > c_{\text{Cu}}:c_{\text{Pb}} > 1:246$; $223:1 > c_{\text{Pb}}:c_{\text{Cd}} > 1:229$. Zn can be practically determined in the presence of Cd at all the concentration ratios. $\Delta E_{\text{p Cu-Pb}} = 246$; $\Delta E_{\text{p Pb-Cd}} = 217$; $\Delta E_{\text{p Cd-Zn}} = 346$.

Fe, Mn: $177:1 > c_{\text{Fe}}:c_{\text{Mn}} > 1:201$; $\Delta E_{\text{p Fe-Mn}} = 163$.

Co, Ni: $282:1 > c_{\text{Ni}}:c_{\text{Co}} > 1:219$; $\Delta E_{\text{p Ni-Co}} = 188$.

Sn, Sb, Bi: Bi and Sn can be practically determined at all the concentration ratios. $\Delta E_{\text{p Bi-Sn}} = 352$; $123:1 > c_{\text{Sn}}:c_{\text{Sb}} > 1:115$; $\Delta E_{\text{p Sn-Sb}} = 127$.

The above mentioned concentration ratios have also been confirmed by mono- and bivariate data analysis^{26,27}, which permitted reliable decision on the presence or absence of interference. In monovariate analysis the interference of a second element is neglected; it is considered, however, in bivariate analysis. In fact, the interference is excluded when slopes of the calibration function of a given element in the mixture are equal to those in the absence of the other element, and, particularly, when the slope of the calibration function related to the interfering element is negligible.

Standard Addition Method in the Case of Mutual Interference

However, an interesting aspect of the analytical procedure proposed is evidently the possibility of determining the metal of a lower concentration and with an unfavourable concentration ratio. In such a case, the standard addition method permitted the extension of the analysis beyond the concentration ratio intervals within which the interference did not exceed the accepted error level of 5%.

Bringing the concentration ratio within the interval valid for mono- and bivariate analysis by adding a metal standard solution of the lower concentration allowed the determination of the metal itself. In fact, the peak cur-

rent *versus* concentration plot of the element having in the mixture lower concentration was nonlinear after the initial standard additions; linearity however, was attained as soon as the concentration ratio of metals was within the validity range of mono- and bivariate analysis. The extrapolation of the linear portion of the curve permitted the evaluation of the concentration of the element present at the lower concentration with good precision and accuracy²⁸⁻³⁰.

As an example, a voltamogram shown in Fig. 1 and Fig. 2 with the relevant analytical calibration function illustrate the interference of Sn in the determination of Sb.

The limit within which linearity prevails was statistically evaluated by the method of Liteanu *et al.*^{31,32} using the t-test criterion.

Once established for aqueous reference solutions, the methods were transferred to the standard reference material in order to confirm the applicability of the analytical procedure.

The analytical results relevant to the standard reference materials obtained by voltammetric technique are reported in Tables I-III.

They show that the certified concentrations of the element, for all the standard reference materials and for all the metals, fall in the confidence interval of the determined concentrations. Then, such experimental data show to have good precision and accuracy. In fact, in all cases, the preci-

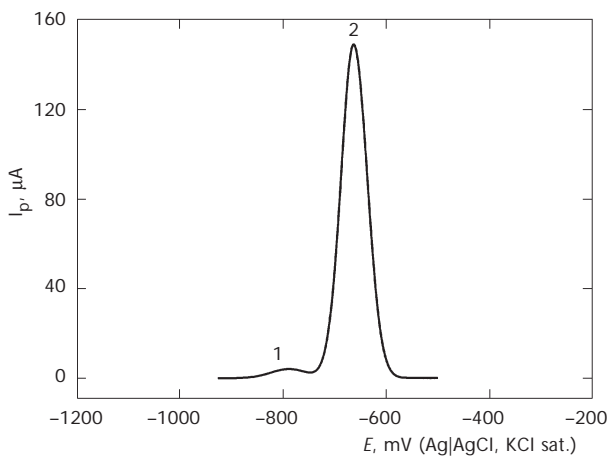


FIG. 1

Differential pulse anodic stripping voltammogram of a mixture containing antimony (peak 1) and tin (peak 2). Concentrations ($\mu g l^{-1}$): 9.6×10^3 (Sn); 23.0 (Sb). $c_{Sn}:c_{Sb} = 417.4$. Experimental conditions are given in the text

TABLE I
Commercial bronze A NIST-SRM 1115. The determined concentrations are the mean of 5 independent measurements \pm s.d., confidence level 99% (concentrations in mg g^{-1})

Metal	Certified concentration	Voltammetry			Spectroscopy		
		determined concentration	$e, \%$	$s_r, \%$	determined concentration	$e, \%$	$s_r, \%$
Cu	879.6	858.1 ± 38.6	-2.4	3.7	849.4 ± 43.0	-3.4	3.7
Pb	0.13	0.12 ± 0.02	-7.7	4.9	0.12 ± 0.02	-7.7	5.1
Cd	-	-	-	-	-	-	-
Zn	117.3	123.0 ± 5.8	+4.9	3.8	112.7 ± 5.3	-3.9	4.3
Fe	1.30	1.38 ± 0.05	+6.2	3.7	1.23 ± 0.08	-5.4	4.5
Mn	-	-	-	-	-	-	-
Co ^a	6.9	7.1 ± 0.3	+2.9	4.0	7.3 ± 0.5	+5.8	3.4
Ni	0.74	0.77 ± 0.04	+4.1	5.1	0.69 ± 0.05	-6.8	4.9
Sn	1.00	0.95 ± 0.1	-5.0	4.2	0.94 ± 0.1	-6.0	5.2
Sb	-	-	-	-	-	-	-
Bi	-	-	-	-	-	-	-

^a Concentration added.

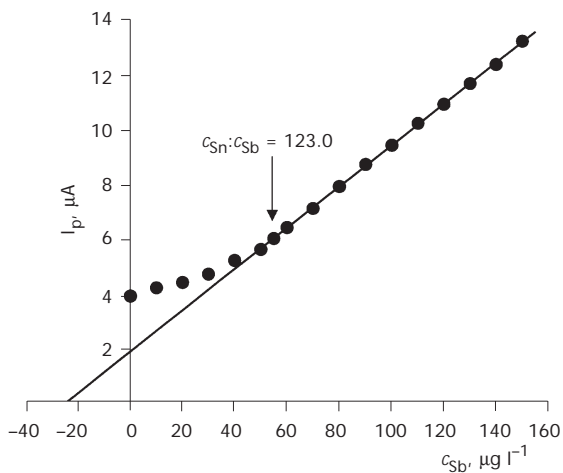


FIG. 2

Analytical calibration function for the determination of antimony in an antimony-tin mixture by differential pulse anodic stripping voltammetry. Concentrations and experimental conditions are given in the caption to Fig. 1

sion, expressed as relative standard deviation (s_r), and the accuracy, expressed as relative error (e), were generally lower than 6%.

Comparison with Spectroscopic Measurements

To validate better the voltammetric analytical procedure proposed, concentrations of all the elements in each standard reference material have been independently determined by atomic absorption spectroscopy. The results reported in Tables I–III represent the experimental confirmation of such a validation. The agreement between the voltammetric and spectroscopic data is certainly very good (differences lower than 6% for all the elements).

Limits of Detection

The limits of detection (LOD) are expressed according to the International Union of Pure and Applied Chemistry²⁴ (IUPAC) and correspond to a probability of 95%²⁵.

TABLE II

Gunmetal BCS-CRM 207/2. The determined concentrations are the mean of 5 independent measurements \pm s.d., confidence level 99% (concentrations in mg g^{-1})

Metal	Certified concentration	Voltammetry			Spectroscopy		
		determined concentration	e , %	s_r , %	determined concentration	e , %	s_r , %
Cu	873.5	840.1 ± 45.3	-3.8	3.9	910.9 ± 42.3	+4.3	4.7
Pb	7.0	6.9 ± 0.2	-1.4	3.1	6.6 ± 0.4	-5.7	4.5
Cd	-	-	-	-	-	-	-
Zn	16.0	15.5 ± 0.7	-3.1	3.0	16.6 ± 0.8	+3.8	4.9
Fe	0.29	0.30 ± 0.03	+3.4	3.8	0.30 ± 0.02	+3.4	4.3
Mn	-	-	-	-	-	-	-
Co ^a	6.9	7.0 ± 0.2	+1.4	3.6	6.6 ± 0.4	-4.3	3.6
Ni	2.8	2.7 ± 0.3	-3.6	4.3	2.6 ± 0.4	-7.1	3.8
Sn	97.4	92.3 ± 5.9	-5.2	3.4	102.1 ± 6.9	+4.8	5.1
Sb	1.00	1.05 ± 0.08	+5.0	4.1	1.06 ± 0.09	+6.0	4.8
Bi	0.40	0.38 ± 0.05	-5.0	4.6	0.39 ± 0.03	-2.5	3.7

^a Concentration added.

The detection limit has been always calculated employing the analytical calibration functions of each metal in all the standard reference material samples²⁵. Such method, once fixed the confidence level (in the present case $K = 3$, confidence level 95% is fixed), allows to determine the limit of detection of the analytical procedure, employing the standard deviation $s_{y/x}$ and the analytical sensitivity b , using the equation: $LOD = Ks_{y/x}/b$.

If the metal was not present in the standard reference material, the analytical calibration function was equally calculated by standard additions to the digest solution and the relevant limit of detection determined.

Table IV reports the limits of detection of each metal in all the standard reference materials and for both instrumental techniques.

Voltammetry or Spectroscopy: Critical Comparison

At the end, a comparison between the two techniques employed can be made, considering both the analytical and technical parameters (Table V).

TABLE III

High tensile brass BCS-CRM 390. The determined concentrations are the mean of 5 independent measurements \pm s.d., confidence level 99% (concentrations in mg g^{-1})

Metal	Certified concentration	Voltammetry			Spectroscopy		
		determined concentration	e, %	s_r , %	determined concentration	e, %	s_r , %
Cu	571.0	596.1 ± 27.2	+4.4	3.8	600.3 ± 35.7	+5.1	4.7
Pb	10.4	9.9 ± 0.6	-4.8	4.3	11.0 ± 0.8	+5.8	4.9
Cd	0.11	0.10 ± 0.001	-9.1	2.9	0.10 ± 0.01	-9.1	3.6
Zn	386.0	369.2 ± 2.0	-4.4	3.7	405.6 ± 2.3	+5.1	4.2
Fe	8.3	7.9 ± 0.6	-4.8	3.9	8.6 ± 0.8	+3.6	2.6
Mn	13.0	13.7 ± 0.8	+5.4	4.2	13.6 ± 0.7	+4.6	3.9
Co ^a	6.9	6.7 ± 0.2	-2.9	4.0	6.5 ± 0.5	-5.8	4.3
Ni	0.33	0.31 ± 0.03	-6.1	4.5	0.32 ± 0.03	-3.2	5.0
Sn	3.4	3.6 ± 0.2	+5.9	3.4	3.5 ± 0.2	+2.9	4.1
Sb	-	-	-	-	-	-	-
Bi	-	-	-	-	-	-	-

^a Concentration added.

TABLE IV

Limits of detection in the standard reference materials employing voltammetric and spectroscopic techniques. The concentrations (calculated as $\mu\text{g l}^{-1}$, expressed in mg g^{-1}) are the mean of 5 independent measurements \pm s.d., confidence level 99%. The limits of detection are expressed according to IUPAC (probability level 95%, $K = 3$)²⁴ and are calculated from the analytical calibration functions of each element ($\text{LOD} = Ks_{y/x}/\text{slope of calibration function}$)²⁵. For instrumental parameters see the text

Metal	Voltammetry			Spectroscopy		
	commercial bronze A NIST-SRM 1115	gunmetal BCS-CRM 207/2	high tensile brass BCS-CRM 390	commercial bronze A NIST-SRM 1115	gunmetal BCS-CRM 207/2	high tensile brass BCS-CRM 390
Cu	0.049 ± 0.002	0.040 ± 0.003	0.053 ± 0.004	0.042 ± 0.004	0.041 ± 0.003	0.048 ± 0.004
Pb	0.023 ± 0.003	0.025 ± 0.002	0.028 ± 0.003	0.025 ± 0.002	0.028 ± 0.001	0.032 ± 0.003
Cd	0.011 ± 0.001	0.015 ± 0.001	0.014 ± 0.001	0.012 ± 0.002	0.018 ± 0.001	0.021 ± 0.002
Zn	0.041 ± 0.003	0.048 ± 0.003	0.055 ± 0.003	0.047 ± 0.003	0.050 ± 0.004	0.062 ± 0.004
Fe	0.069 ± 0.004	0.077 ± 0.006	0.084 ± 0.006	0.075 ± 0.005	0.083 ± 0.003	0.088 ± 0.005
Mn	0.081 ± 0.006	0.079 ± 0.005	0.089 ± 0.008	0.086 ± 0.004	0.087 ± 0.005	0.095 ± 0.008
Co	0.058 ± 0.004	0.069 ± 0.005	0.077 ± 0.005	0.064 ± 0.006	0.065 ± 0.006	0.081 ± 0.007
Ni	0.044 ± 0.003	0.049 ± 0.003	0.058 ± 0.004	0.050 ± 0.004	0.048 ± 0.006	0.063 ± 0.005
Sn	0.060 ± 0.005	0.069 ± 0.004	0.075 ± 0.004	0.071 ± 0.006	0.079 ± 0.005	0.087 ± 0.005
Sb	0.065 ± 0.006	0.073 ± 0.003	0.082 ± 0.007	0.077 ± 0.009	0.082 ± 0.006	0.088 ± 0.008
Bi	0.077 ± 0.004	0.086 ± 0.007	0.092 ± 0.009	0.076 ± 0.007	0.085 ± 0.008	0.096 ± 0.006

TABLE V

Voltammetry and spectroscopy: a comparison

	Voltammetry	Spectroscopy
Sample mineralization	yes	yes
Matrix modifier	no	yes
Simultaneous determination	yes	no
Signal interference	possible	no
Accuracy (e , %)	generally < 6	generally < 6
Precision (s_p , %)	generally < 5	generally < 5
Selectivity	possible interference	no interference
Equipment cost	lower	higher

As to the precision, accuracy and limit of detection, good and comparable results can be observed in all cases using the two techniques, which are then equivalent. The voltammetry however, is better compared with spectroscopy, which allows simultaneous metal determinations, does not require the addition of matrix modifiers and it is much less expensive.

CONCLUSIONS

Voltammetry is certainly a valid analytical technique, relatively simple, fast and suitable for the simultaneous determination of metals in multi-component complex matrices such as copper alloys, showing good precision and accuracy. It exhibits also satisfactory high sensitivity, allowing to obtain very low limits of detection.

In voltammetric determinations, the standard addition method allows to simultaneous determination of more elements also in the case of strong interference and of signal overlapping.

Such a technique may be certainly a good alternative to spectroscopy, which requires rather expensive equipment.

SYMBOLS

E_a	adsorption potential (V/Ag, AgCl, saturated KCl)
E_d	deposition potential (V/Ag, AgCl, saturated KCl)
E_f	final potential (V/Ag, AgCl, saturated KCl)
E_i	initial potential (V/Ag, AgCl, saturated KCl)
E_p	experimental peak potential (V/Ag, AgCl, saturated KCl)
ΔE_p	peak potential difference between plots of two elements, mV
ΔE	pulse amplitude, mV
dE/dt	potential scan rate, mV s ⁻¹
f	pulse repetition, s
t	purging time prior to electrolysis, s
t_a	adsorption time, s
t_d	electrolysis time, s
t_r	rest time before the starting of the scan rate, s
t_s	sampling time, ms
u	stirrer speed, rpm
v	pulse duration, ms
DPV	differential pulse voltammetry
DPASV	differential pulse anodic stripping voltammetry
DPAdSV	differential pulse adsorption stripping voltammetry
s.d.	standard deviation

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