

THE DETERMINATION OF COPPER BY FLOW INJECTION ANALYSIS WITH FLAME AAS DETECTION AFTER PRECONCENTRATION BY SOLVENT EXTRACTION

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Trace amounts of copper ($\rho_{\text{Cu}} = 2$ to 900 mg ml^{-1}) were determined by FIA-FAAS after extraction of the Cu chelate with ammonium pyrrolidine dithiocarbonylate (APDC), present in a concentration of $\rho_{\text{APDC}} = 1 \text{ mg ml}^{-1}$, from 0.2M acetate buffer at pH 5.05 into 4-methyl-2-pentanone. The limit of determination was $L_Q = 2 \text{ ng ml}^{-1}$ for the injection of $150 \mu\text{l}$ of the organic phase into a continuous stream of air as the carrier medium. The maximum throughput was about 40 samples per hour. The method was applied to the determination of copper in water samples from power station cooling circuits.

Ammonium pyrrolidine dithiocarbonylate (henceforth APDC), which forms stable chelates with ions of more than thirty metals over a wide pH region¹, has proved convenient for the preconcentration of trace amounts of metals from aqueous solutions by solvent extraction. An asset of APDC as compared to other reagents is in its higher stability in acid solutions^{1,2}. Over the wide pH range from 0.5 to 9, copper is extracted quantitatively³ with 4-methyl-2-pentanone (methyl isobutyl ketone, MIBK), which is among the most popular organic solvents for the extraction of metal chelates with APDC because it satisfies best the requirements put on organic solvents for FAAS (ref.⁴).

The classical procedures of solvent extraction are highly time consuming, and therefore the in-line combination of this technique with flow injection analysis finds ever-increasing application⁵⁻⁷. This brings about a higher sample throughput, lowering in the sample and reagent volumes, possibility of analyzing samples with high inert salt contents, reduction in the interfering matrix effect, and last but not least, increase in the sensitivity and, to some extent, accuracy of the results⁵⁻⁷.

In the present work, the parameters of a FIA-FAAS apparatus for the solvent extraction and of the FAAS detecting system using acetylene-air flame were optimized. A procedure was worked out for the determination of trace concentrations of copper after its preconcentration by solvent extraction of its chelates with APDC into MIBK from acetate buffer at pH 5.

EXPERIMENTAL

Chemical and Apparatus

Standard solution of Cu(II) at a concentration of 953 mg l^{-1} in 0.1M-HNO_3 was prepared by dissolving copper metal (99.96%; Lachema, Brno) in concentrated HNO_3 and diluting with bidistilled water. The solution was standardized by chelometric titration with EDTA using murexide as the indicator. Working solutions containing copper in concentrations of 0.001 to $2 \text{ } \mu\text{g ml}^{-1}$ were prepared in acetate buffer at pH 5.05, ionic strength $I = 0.14$.

Fresh aqueous solutions of ammonium pyrrolidine dithiocarboxylate in a concentration of 1 g l^{-1} were prepared from the chemical of reagent grade purity (B. D. H., Poole, U.K.) and purified by extraction with small volumes of MIBK of reagent grade purity (Loba Chemie, Vienna, Austria); after phase separation, the aqueous solution of APDC was filtered out.

The other chemicals used were commercial products of p.a. or p.p. purity (Lachema, Brno). Bidistilled water was prepared in a quartz still. Sodium acetate was purified by extraction with 1-PAN into MIBK. The carrier media were bidistilled water, aqueous ethanol ($\varphi_{\text{EtOH}} = 20\%$), MIBK saturated with water or air.

Detection of Cu(II) was performed on a PE 306 atomic absorption spectrometer (Perkin-Elmer, Norwalk, U.S.A.) equipped with an Intensitron hollow cathode lamp (current 15 mA) operated at the wavelength of the copper resonance line, 324.8 nm ; slit width was 0.7 nm . A 10 cm one-slot burner was used for measurements in the acetylene-air flame; the flow rates of the two gases were 3.6 and 22.5 l min^{-1} , respectively, for aqueous Cu(II) solutions, and 1.1 and 15.0 l min^{-1} , respectively, for solutions of the chelate in organic solvents. The absorption signal was scanned on a TZ 4 100 line recorder (Laboratorní přístroje, Prague). Acidity of the aqueous solutions was measured with an OP 208 pH-meter equipped with an OP 0808P combined electrode (Radelkis, Budapest, Hungary).

The FIA-FAAS equipment with in-line solvent extraction (Fig. 1) comprised S 32 peristaltic pumps (Donet, Poland) with polypropylene or polyethylene tubing 1 mm i.d. , a reaction (mixing) coil and an extraction coil, both made from Teflon capillaries 0.6 mm i.d. (Norton Chemplast, Wayne, U.S.A.), an Y type Teflon segmentor with inlet and outlet channels 0.6 mm i.d. , a phase separator, an injecting device and a FAAS detector.

The phase separator (Fig. 2) was formed by two Teflon blocks $60 \times 26 \times 11 \text{ mm}$, each provided with a groove 41 mm long, 1.2 mm broad and $0.05\text{--}0.5$ or $0.02\text{--}0.2 \text{ mm}$ deep. Between the grooves was inserted a $48 \times 11 \text{ mm}$ membrane made from 1 PS hydrophobized cellulose (Whatman, F.R.G.) or from Zitex 47-M Medium Teflon (Norton Chemplast, Wayne, U.S.A.).

Solutions of sample (S) and chelating agent (R) were pumped continuously through the mixing piece (M) and the mixing and reaction coil (MRC) to the segmentor (T). The organic solvent was pumped to the segmentor continuously either directly by the peristaltic pump (P) with a polyethylene pumping tube lined with a Teflon capillary, or by means of a displacing bottle (DB) from which MIBK was displaced by overpressure of water. At higher flow rates of the aqueous phase, however, irregularities appeared in the segmentation of the flow of the two phases after the segmentor.

The extraction of the chelate from the aqueous phase into the organic solvent in the segmented flow with segment lengths $2\text{--}3 \text{ mm}$ took place in the extraction coil (EC), interconnecting the segmentor and the phase separator (PS). The separated organic phase was fed to the loop injector (LI) having a variable volume of 20 to $300 \text{ } \mu\text{l}$. After filling the loop injector, the Cu-APDC chelate in MIBK was injected into the continuous stream of the carrier medium (C) and transported to the nebulizer of the FAAS device. A pulse-free continuous flow of the carrier medium at the optimum flow rate was provided by hydrostatic pressure of the liquid in an infusion bottle placed

approximately 1 m above the nebulizer, in conjunction with the natural aspiration rate of the nebulizer; the peristaltic pump was employed occasionally.

Method

The lowest flow rates of the aqueous phase, $Q_{aq} = Q_R + Q_S = 1.6 \text{ ml min}^{-1}$, and of the organic phase $Q_{org} = 0.6 \text{ ml min}^{-1}$, were applied to the optimization of the FIA-FAAS system. The flow rate of the aqueous phase was composed of that of the sample (Q_S) and that of the chelating agent (Q_R) before the segmentor, which were 0.8 ml min^{-1} each. The extraction coil length was usually $L_e = 390 \text{ cm}$, the length of the outflow capillary of the phase separator for transporting the organic phase to the injecting device was $L_i = 23 \text{ cm}$ and the length of the limiter for the outflow of the aqueous phase from the phase separator was 100 cm . The mixing coil length $L_m = 45 \text{ cm}$ ensured a quantitative formation of the Cu-APDC chelate. The injected volume of the extract V_S was 100 or 150 μl . The injecting device was interfaced to the nebulizer via a $150 \times$

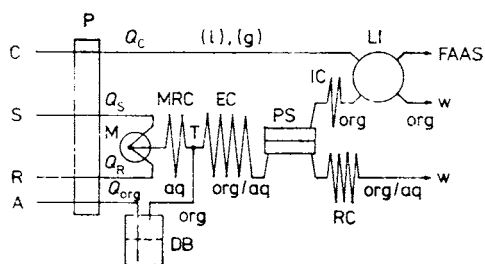


FIG. 1

Layout of the FIA-FAAS apparatus involving solvent extraction. C carrier medium, S sample, R solution of APDC, A water, P peristaltic pump, M mixing piece, DB displacement bottle, MRC mixing-and-reaction coil (length L_m), EC extraction coil (L_e), T segmentor, PS phase separator, LI loop injector, IC interconnecting capillary (L_i), RC restricting coil (L_g), FAAS flame AAS detector, W waste, aq aqueous phase stream, org organic phase stream, Q_c , Q_s , Q_R , Q_{aq} , Q_{org} flow rates of carrier medium, Cu(II) sample, reagent (APDC), aqueous and organic phases, respectively, (l), (g) liquid or gaseous carrier stream

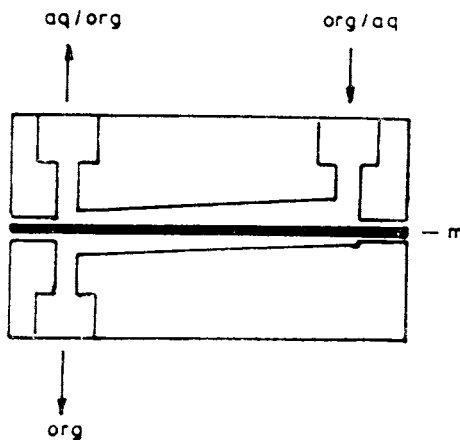


FIG. 2

Layout of the phase separator with a membrane; org/aq segmented flow of organic and aqueous phases, aq/org flow of aqueous phase with residues of unseparated organic phase, org separated organic phase, m separating membrane

× 0.6 mm capillary. The aspiration rate of the nebulizer was held at 6.6, 6.8 or 4.4 ml min⁻¹ for water, MIBK and aqueous ethanol, respectively.

Calibration curves and other dependences were obtained by measuring the peak heights and converting them to absorbance values. The calibration curves were evaluated by using the least squares method. The slopes were also determined from the coordinate ratios y/x in the reference point for $A \rightarrow 0$.

The limit of determination L_Q was identified with the concentration of copper (in ng ml⁻¹) giving rise to the absorbance $A = A_{b1} + 10s_{b1}$ where A_{b1} is the average value of absorbance and s_{b1} , its standard deviation, for 10 independent measurements on a blank solution.

RESULTS AND DISCUSSION

The performance of the phase separator was evaluated in terms of the ratio of the volume of the separated organic phase passed through the separating membrane to that of the unseparated organic phase leaving the separator together with the aqueous phase through the limiter ($L_g = 50$ to 150 cm for $L_i = 15$ or 23 cm) to the waste.

The amount of the separated organic phase increased with increasing length of the limiter L_g for membranes of both types (Fig. 3). At $L_g > 100$ cm, the aqueous phase also began to pass through the membranes, bringing about lowering in the absorbance of the organic phase. A marked improvement in the separating efficiency was achieved by using two layers of the hydrophobized cellulose membrane. The resulting efficiency at $L_g = 150$ cm increased to 74 and 78% for $L_i = 15$ and 23 cm, respectively.

The service life of a pair of cellulose membranes in the phase separator was 10–12 hours of performance of the extraction system at the minimum flow rates of the two phases, 0.6 and 1.6 ml min⁻¹, respectively. After surpassing this time, the separating efficiency dropped rapidly and droplets of the aqueous phase appeared in the organic phase.

The Teflon membranes exhibited better properties. The resulting separating efficiency, 84 and 87% at $L_i = 15$ and 23 cm, respectively ($L_g = 100$ cm), was higher also at a lower pressure gradient. The quality of the membrane was good for a minimum of four weeks of performance (about 100 h).

The further measurements were performed with a Teflon membrane, which at the optimum capillary lengths ($L_g = 100$ cm, $L_i = 23$ cm) ensured a constant pressure gradient at the membrane, without the hazard of penetration of the aqueous phase into the separated organic phase at the chosen flow rates of the two phases.

The dependence of the absorbance signal on the mixing (reaction) coil length L_m for the continuous injection of solutions with $\rho_{Cu} = 2 \mu\text{g ml}^{-1}$ and $\rho_{APDC} = 1 \text{ mg ml}^{-1}$ via the mixing piece revealed that the reaction was very rapid. The change in the absorbance signal was very low (about 4.5%) over the region of $L_m = 11$ –78 cm (nearly nil over the 45–78 cm range). The minimum length chosen, $L_m = 45$ cm, ensured a quantitative reaction yield and minimal dispersion of the reaction mixture band.

The extracting efficiency of the FIA equipment increased considerably with increasing length of the extraction coil up to $L_e = 340$ cm (Fig. 4). Additional extension of the extraction coil only led to an approximately 4% absorbance rise while the hydrodynamic resistance of the device increased substantially. The absorbance of the organic phase (for the injection of both 100 or 150 μ l of the organic phase), was about 20% higher over the entire measurement region if the Cu-ADPC chelate was injected into aqueous ethanol than if it was injected into the flow of water.

Increase in the flow rate of the aqueous phase Q_{aq} over the region of 1.6 to 8 $\text{ml} \cdot \text{min}^{-1}$ at a constant ratio of the flow rates of the Cu(II) and APDC solutions ($Q_{Cu} = 0.5 \mu\text{g ml}^{-1}$, $Q_{APDC} = 1 \text{ mg ml}^{-1}$) and at $Q_{org} = 0.6 \text{ ml min}^{-1}$ (Fig. 5) brought about increase in the absorbance of the organic phase owing to the concentration of the Cu-APDC chelate from the larger volume of the aqueous phase to the (constant) small volume of the organic phase: for $Q_{aq} = 1.6, 2.2, 2.8-5.2$ and $5.2-8.0 \text{ ml min}^{-1}$, R was 96.2, 94.3, 90.5 and 88.1%, respectively.

The degree of concentration is given by the ratio Q_{aq}/Q_{org} . These values, however, can be somewhat different from the actual ones because all flow rates are measured prior to interfacing the separator to the extraction coil.

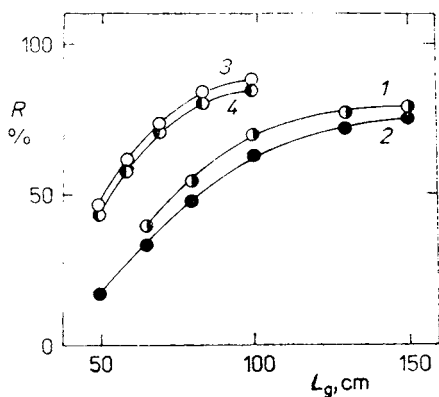


FIG. 3

Effect of limiter length L_g on the separating efficiency R (in % passed organic phase) for separating membranes from hydrophobized cellulose (curves 1, 2) and Teflon (curves 3, 4); $V_{org} = 100 \mu\text{l}$, $L_e = 300$ cm, $Q_{org} = 0.6 \text{ ml min}^{-1}$, $Q_{aq} = 1.6 \text{ ml min}^{-1}$, $Q_{Cu} = 2 \mu\text{g ml}^{-1}$, $Q_{APDC} = 1 \text{ mg ml}^{-1}$, $L_i = 23$ cm (curves 1, 3) or 15 cm (curves 2, 4)

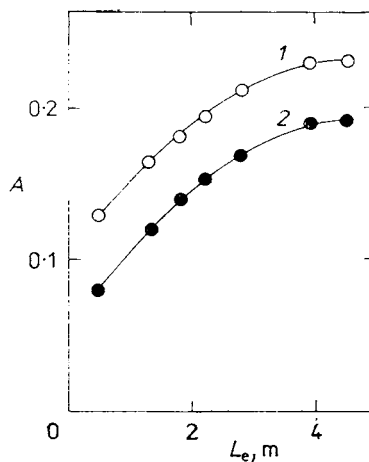


FIG. 4

Dependence of absorbance of the organic phase on the extraction coil length L_e ; $Q_{Cu} = 2 \mu\text{g ml}^{-1}$, $Q_{APDC} = 1 \text{ mg ml}^{-1}$, $Q_{org} = 0.6 \text{ ml min}^{-1}$, $Q_{aq} = 1.6 \text{ ml min}^{-1}$, $V_{org} = 100 \mu\text{l}$. Carrier medium: 1 ethanol ($\phi = 20\%$), 2 water

At $Q_{\text{aq}} > 8 \text{ ml min}^{-1}$ the aqueous phase began to penetrate through the separating Teflon membrane due to the lowered separating efficiency. A flow rate of the aqueous phase $Q_{\text{aq}} = 7.2 \text{ ml min}^{-1}$ was chosen for the measurements; this corresponded to the degree of concentration $Q_{\text{aq}}/Q_{\text{org}} = 12$ and increase in the sensitivity of determination approximately 15 or 30 times as compared to the direct nebulization of aqueous solutions of sample at the same concentration (with respect to ρ_{Cu} in the initial sample solution or in the sample solution after quantitative mixing with the solution of APDC in the mixing coil).

When the organic phase with the Cu-APDC chelate was injected, the absorbance signal increased with increasing volume injected up to $150 \mu\text{l}$ (Fig. 6). Further increase in this volume up to $300 \mu\text{l}$ was only accompanied by a minor increase in the signal, viz. 9.2, 5.1, 11.8 and 2.9% for water, aqueous ethanol, MIBK and air as the carrier media, respectively. The highest absorbance signal, and hence the maximum sensitivity, was achieved using air as the carrier medium.

The time consumed for filling the 100, 150 and $300 \mu\text{l}$ volumes of the injection loop in the FIA-FAAS equipment was 40, 60 and 120 s, respectively. For time-saving

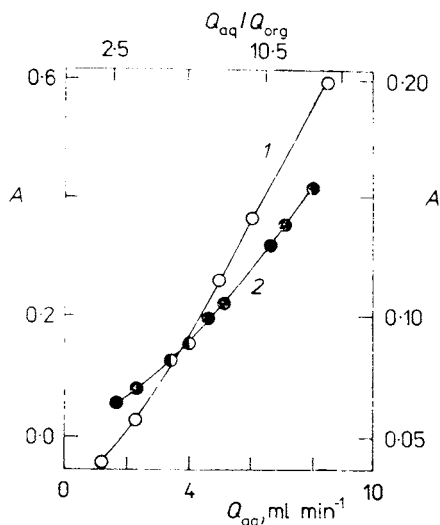


FIG. 5

Dependence of absorbance of the organic phase on the flow rate of the aqueous phase; $\rho_{\text{Cu}} = 0.5 \mu\text{g ml}^{-1}$, $\rho_{\text{APDC}} = 1 \text{ mg ml}^{-1}$, $Q_{\text{org}} = 0.6 \text{ ml min}^{-1}$, $V_{\text{org}} = 100 \mu\text{l}$, carrier medium: air. 1 hydrophobized cellulose membrane (2 layers) (right-hand axis), multiply Q_{aq} by 0.6; 2 Teflon membrane (left-hand axis)

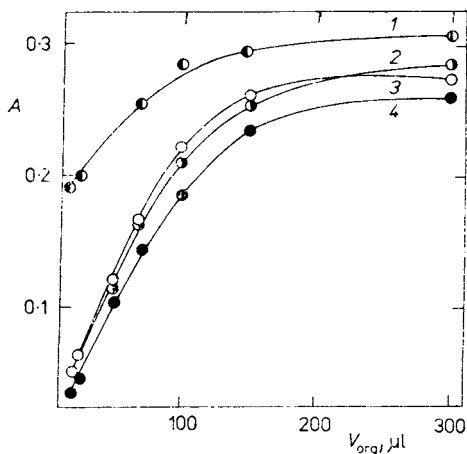


FIG. 6

Dependence of absorbance of the organic phase on the injected volume of Cu-APDC extract in MIBK; $\rho_{\text{Cu}} = 2 \mu\text{g ml}^{-1}$, $\rho_{\text{APDC}} = 1 \text{ mg ml}^{-1}$, $Q_{\text{aq}} = 1.6 \text{ ml min}^{-1}$, $Q_{\text{org}} = 0.6 \text{ ml min}^{-1}$, $L_e = 340 \text{ cm}$, $L_i = 23 \text{ cm}$. Carrier medium: 1 air, 2 MIBK, 3 ethanol ($\varphi = 20\%$), 4 water

reasons, only 100 or 150 μl of the organic phase was fed to the nebulizer, although 3 to 10% of the absorbance signal was thereby sacrificed.

The absorbance signal was also affected by the aspiration rate of the nebulizer (Fig. 7). The differences in the signal were rather marked if organic phase volumes larger than 100 μl were injected and MIBK was used as the carrier medium.

If the organic phase was nebulized, the composition of the flame had to be altered as compared to that used for aqueous solutions⁷. The absorbance signal, as well as the sensitivity of the determination, increased with lowering flow rate of acetylene for all carrier media studied. The lowest acetylene flow rate, 0.9 l min^{-1} , was achieved when using MIBK, because this substance served also as fuel. Water, on the other hand, cooled the flame, extinguishing it at acetylene flow rates lower than 1.2 l min^{-1} .

The highest absorbance signals, over the entire range of acetylene flow rates, were obtained by injecting the chelate solution in the organic phase into air as the carrier medium. With aqueous ethanol, MIBK or water as the carrier media the absorbance signal was 20, 23 and 33%, respectively, lower over the entire region of acetylene flow rates used (0.8 to 2.0 l min^{-1}).

The calibration curves were strictly linear over the concentration regions of $\rho_{\text{Cu}} = 20\text{--}900$ and $2\text{--}500$ ng ml^{-1} for 100 and 150 μl volumes, respectively, of the organic phase injected into the continuous stream of aqueous ethanol or air; this applied to both of the flow rates of the aqueous phase $Q_{\text{aq}} = 1.6$ and 7.2 ml min^{-1} at the optimum parameters of the FIA-FAAS equipment.

When the organic phase (150 μl) was injected into the flow of air or aqueous ethanol at $Q_{\text{aq}} = 7.2$ ml min^{-1} , the sensitivity of determination was 17 and 11 times, respectively, higher than if the aqueous solutions of Cu(II) samples used for the extraction were directly nebulized.

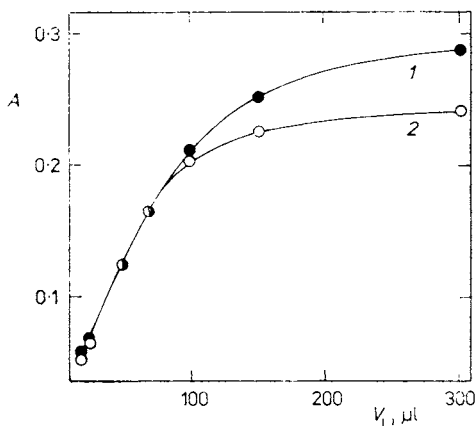


FIG. 7

Dependence of absorbance of the organic phase on the injected volume of Cu-APDC extract in MIBK; $\rho_{\text{Cu}} = 2$ $\mu\text{g ml}^{-1}$, $\rho_{\text{APDC}} = 1$ mg ml^{-1} , $Q_{\text{aq}} = 1.6$ ml min^{-1} , $Q_{\text{org}} = 0.6$ ml min^{-1} , $L_e = 340$ cm, carrier medium: MIBK. Nebulizer aspiration rate (ml min^{-1}): 1 6.8, 2 4.2

The limit of determination, $L_Q = 2 \text{ ng ml}^{-1}$ (determined from the calibration curves for the concentration region of $c_{\text{Cu}} = 2 - 50 \text{ ng ml}^{-1}$), is approximately 5 times better than as obtained by direct nebulization of aqueous solutions of Cu(II) ions without preconcentration ($L_Q = 10 \text{ ng ml}^{-1}$), but approximately 7 times poorer than as obtained in the same experimental conditions on the same FIA-FAAS equipment applying the method of preconcentration of copper on microcolumns of chelating sorbents ($L_Q = 0.3 \text{ ng ml}^{-1}$)⁸.

The recovery from the determination of copper at a concentration of $0.5 \text{ } \mu\text{g ml}^{-1}$ with a standard addition of copper in a concentration of $0.1 \text{ } \mu\text{g ml}^{-1}$ was from 98.5% for the medium of 0.63M-HCl (pH 0.96) to 100% for redistilled water (pH 6.72) or 0.2M acetate buffer (pH 5.24). By the method of standard addition of copper in the above concentration, the separating efficiency was verified for copper in a concentration of $0.5 \text{ } \mu\text{g ml}^{-1}$ from 2M-NaNO₃ or NaCl (recovery 99.6 and 99.9%, respectively). The relative standard deviations lay in the region of $s_r = 1.57 - 2.72\%$.

This method for the determination of trace concentrations of copper ions by extraction of its chelates with APDC into MIBK by the FIA-FAAS technique was applied to the determination of copper in high purity waters from the secondary cooling circuit of a nuclear power station and in samples of drinking water. The data for the cooling waters were in a very good agreement with those obtained by the FIA-FAAS method coupled with preconcentration of the copper ions on microcolumns of the Spheron Oxin 1 000 chelating sorbent⁸.

In conclusion, comparison of the results with those from AAS measurements with electrothermal atomization showed that the attained limit of determination, $L_Q = 2 \text{ ng ml}^{-1}$, is comparable to or better than that achieved by ETA AAS with direct injection of aqueous solutions of Cu(II) ions into the electrothermal atomizer under the same conditions and on the same instrument.

The time of a determination, for the injection of 100 or 150 μl of the organic phase into the nebulizer, was 60 to 90 s, which corresponds to throughputs of 40 to 60 samples per hour. The time of a determination by the ETA AAS method is about 80 s, hence, commensurable with that in the FIA-FAAS method coupled with solvent extraction.

As compared to the FIA-FAAS method involving preconcentration on microcolumns of a chelating sorbent, the limit of detection is poorer; also the work with microcolumns is simpler and more agreeable, especially thanks to the elimination of organic solvents. The throughput of the two preconcentration methods is approximately the same.

Against the classical procedures of separation and preconcentration by solvent extraction on a macrochemical scale, the FIA-FAAS method in-line coupled with the extraction system features a considerable reduction in the time demand and consumption of the sample as well as reagents. Of importance is also the appreciable lowering in the laboratory air pollution by organic vapours, the whole system

working in a closed cycle preventing free evaporation of the substances involved.

Solvent extraction combined with the FIA-FAAS technique is convenient particularly when handling samples with a complex matrix from which analyte has to be separated (biological matter, sea water, etc.). In such instances this technique can serve as an alternative to ETA AAS.

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