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PRECONCENTRATION AND ATOMIC ABSORPTION DETERMINATION OF COPPER TRACES IN WATERS BY ON-LINE ADSORPTION-ELUTION ON AN ACTIVATED CARBON MINICOLUMN

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Summary—A continuous preconcentration method for the determination of trace copper in waters was developed. Ammonium pyrrolidinedithiocarbamate is used to form a chelate which is adsorbed on an activated carbon minicolumn and desorbed with 200 μl of methyl isobutyl ketone. The organic extract is driven by a water stream to an atomic absorption spectrometer. By using a time-based technique equivalent to from 1.5 to 4.5 ml of sample, preconcentration factors between 35 and 100, respectively, are achieved. The flow system is quite simple and rapid, and provides highly precise results (RSD 1.8–3.5%). The results obtained in the determination of copper in waters show the usefulness of the proposed method.

Activated carbon has been used as a trace collector for multi-element preconcentration in the analysis of waters, high-purity substances, etc. There are two general approaches to metal preconcentration using activated carbon, namely from aqueous solutions by simply adjusting the pH to an adequate value[1,2] and by using a chelating agent.[3–11] A literature scan on water and pure salt analyses revealed that enrichment of heavy metals on activated carbon is usually carried out after chelation with ammonium pyrrolidinedithiocarbamate (APDC),[5] 8-hydroxyquinoline,[6] potassium ethyl xanthate,[7,8] dithizone,[9] chrome azurol S[10] or the ammonium salt of the dithiophosphoric acid 0,0-diethyl ester;[11] also, following desorption in a small volume of nitric acid, the metal concentrations are measured by atomic absorption spectrometry (AAS) or (as slurry) by ICP–AES. The adsorption mechanism of metal chelates on activated carbon (AC) has been investigated by Piperaki *et al.*[3] and Hutchinson *et al.*,[4] who used amino acids and ferroin as ligands, respectively; the former authors[3] found that, as a rule, sorption is quantitative provided the chelate contains π-electrons systems and sulphur atoms, even though chain length and presence of hydrophobic or hydrophilic groups in the organic molecule must also be considered. The latter authors showed the occurrence of two types of sites for adsorption of chelates on activated carbon since carbon surfaces possess two distinct structural features.[4] This type of manual preconcentration technique requires large sample volume (usually 100–1000 ml), is rather time-consuming (it involves reaction, filtration and dissolution) and often gives rise to irreproducible results (variation coefficients of 2.7–33%) arising from the manipulation preceding the analytical measurements; on the other hand, it provides high concentration factors.

The advantages of continuous automatic techniques are particularly attractive when extensive manipulation is involved in a given determination (*e.g.* when a preconcentration technique is required). Continuous preconcentration flow systems have been used in conjunction with AAS to concentrate metals ions. Thus, one continuous extraction system was developed for the automatic preconcentration of copper, nickel, lead and zinc in aqueous samples into methyl isobutyl ketone using ammonium pyrrolidinedithiocarbamate as extractant; an enrichment factor of 15–20 was achieved relative to direct aspiration of aqueous samples.[12] Continuous precipitation-dissolution manifolds have been used for the preconcentration and determination of μg/g amounts of

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copper[13] and cobalt[14] in silicate rocks. Dithioxamide and 1-nitroso-2-naphtol were used as organic precipitating reagent for copper and cobalt, respectively; concentration factors of up to 500 (sample volume, 250 ml) were readily achieved. Two classes of column materials have been used for preconcentration and matrix removal in flow injection analysis, viz. ion exchangers and chelating agents, both covalently bound to a solid support.[15] Preconcentration devices using ion-exchangers for the determination of copper in waters have been widely proposed.[16–21] Some sorbent extraction systems including a C_{18} column have been employed for the determination of traces of copper and lead[22] and cadmium, copper, lead and nickel[23] with diethyldithiocarbamate or 8-quinolinol. In both instances, the preconcentrated chelate was eluted into a small volume of a water-miscible organic solvent (*e.g.* methanol or ethanol), so the eluted analytes underwent some dispersion on their way to the detector; this resulted in somewhat low preconcentration factors between 5 and 20).

The aim of this work was to reduce human involvement in the enrichment of trace copper present in waters by using an activated carbon column as adsorbent. APDC was tested for use as reagent for adsorption on the activated carbon. The chelate was eluted with a small volume (200 μl) of methyl isobutyl ketone. This organic solvent provided better results than other organic and inorganic solutions. A complementary comparative study on the chelate adsorption on the activated carbon column, a filter and a PTFE coil was also made. Finally, various types of water were analysed as samples in order to test the performance of the proposed method.

EXPERIMENTAL

Apparatus

A Perkin-Elmer 380 atomic absorption spectrometer furnished with a hollow-cathode copper lamp was used. The instrument was set at a wavelength of 324.7 nm, and the air/acetylene flame was adjusted according to standard recommendations. The peristaltic pump used was a Gilson-Minipuls-2 model, fitted with poly(vinyl chloride) tubes. Two Rheodyne 5041 injection valves were also used. A Scientific System 05-105 column with a removable screen-type stainless steel filter (pore size 0.5 μm, chamber inner volume 580 μl and filtration area 3 cm^2) and an Omnifit 3303 Teflon filter (low dead volume, 100 μl) were used for filtration. The adsorption minicolumn was made by packing a PTFE capillary (2.5 cm long × 3 mm i.d.) with activated carbon (about 70 mg). Small glass wool beads on the ends prevented material losses. The column was initially flushed with 0.1*N* nitric acid. Subsequent use of methyl isobutyl ketone as eluent during each operational cycle was enough to make it ready for re-use. Peak heights and areas were measured with the aid of a Merck-Hitachi D-2500 Chromato-Integrator.

Reagents

A 1000 mg/l copper solution was prepared by dissolving 1.000 g of the metal in a small volume of concentrated nitric acid and diluting to 1 l with 1% (v/v) nitric acid. A freshly prepared 0.1% (w/v) ammonium pyrrolidinedithiocarbamate (Aldrich, Germany) and methyl isobutyl ketone (Panreac, Spain) were also used. Darco 20-40 activated carbon (Aldrich, Germany) was employed for sorption purposes. All other chemicals used were of analytical reagent grade.

Preparation of standards and samples

Copper solutions containing 2–170 ng/ml of the metal were prepared in 0.1*N* nitric acid. The water samples were analysed on the collection date without pretreatment. Only the river water required filtration through a membrane filter (Millipore 0.45 μm). All samples were acidified with concentrated nitric acid (to avoid dilution), to made 0.1*N* in the acid and introduced directly into the continuous preconcentrating system shown in Fig. 1.

Procedure

The continuous flow manifold used for the preconcentration of copper (II) is depicted in Fig. 1. The sample, containing 2–170 ng/ml of Cu(II) in 0.1*N* nitric acid, was continuously pumped through the manifold for 2 min and thoroughly mixed with the chelating reagent (0.1% APDC). The chelate was retained on the activated carbon column placed in the loop of the injection valve, while the sample matrix was driven to waste (W1). In this step, a water carrier was pumped to the instrument in order to flush the nebulizer after each measurement. In the elution step, after 2 min of sample-reagent continuous pumping, the two injection valves were switched simultaneously, so 200 μl of MIBK solvent was passed through the adsorbed chelate to desorb it and sweep the Cu to the detector. Peak heights or areas were used for analytical measurements. A blank of 0.1*N* nitric acid was also used ($A \approx 0.015$ units).

RESULTS AND DISCUSSION

Activated carbon can be considered an organic collector for preconcentration of trace metals. However, better results are to be expected when the metals are complexed with organic chelating agents prior to adsorption on AC. APDC forms strong, mostly neutral complexes with heavy metals, which can be absorbed onto AC.[5] There are no references to the use of this type of sorbent or reagent for trace enrichment in continuous flow systems; other continuous systems including a C_{18} column use water-miscible solvents for elution, but none employ water-immiscible solvents.[22,23]

Preconcentration

Experiments were carried out by continuously introducing of a solution containing 50 ng/ml of copper into the system. A time-based technique equivalent to using 3.0 ml of sample only (sample flow rate, 1.5 ml/min; pumping time, 2 min) was chosen for this purpose. Methyl isobutyl ketone (MIBK) was used as solvent to elute the adsorbed chelate from the column because no dispersion of the organic extract plug occurred in the aqueous feed stream.

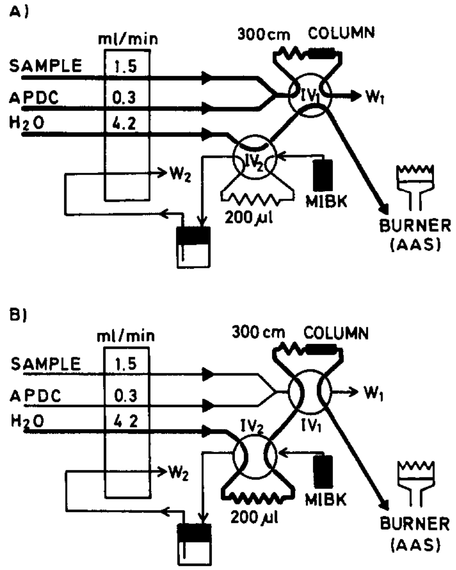

Fig. 1. Flow injection manifold for preconcentration of copper. A and B denote adsorption and elution steps, respectively. The marked broad lines carry relevant streams in the individual stages. IV, Injection valve; W, waste; APDC, ammonium pyrrolidinedithiocarbamate; MIBK, methyl isobutyl ketone.

Maximum chelate adsorption was achieved at a low sample pH (0.7–1.3), but a further plateau was obtained between pH 3.8 and 5.1 in addition to a decrease in the absorbance by about 40% relative to the first plateau. The influence of various acids on the preconcentration reaction was also studied by using samples containing 50 ng/ml of copper at pH 1.0 adjusted with nitric, perchloric, hydrochloric or sulphuric acid; the absorbance in hydrochloric or sulphuric acid decreased by 20 and 40% compared to that in perchloric or nitric acid. It is interesting to note that the first acid zone is unusual in liquid–liquid extraction procedures using this ligand. This suggests that the acidic medium favours retention of the chelate on activated carbon.

The effect of APDC concentration was studied in the range 0.001–1%. The absorbance difference remained constant above 0.005% so a 0.1% concentration of APDC in water was chosen. Replacing the APDC stream with a water stream (the sample was also circulated) resulted in a similar absorbance in the elution step to that obtained by replacing the sample stream with 0.1*N* nitric acid stream (blank) namely between 0.010 and 0.020 units.

The influence of temperatures in the range 20–70°C was also investigated by thermostatting the preconcentration reactor and the column. The analytical signal decreased above 30°C because through decomposition of the copper–APDC complex, so measurements were made at room temperature.

The sample flow-rate (4.0 ml of a solution containing 50 ng/ml copper) resulted in very small variations in the range 1.0–2.0 ml/min. Flow-rates above 2.0 ml/min decreased the signal because the residence time also decreases. Increasing the APDC flow-rate (which would be equivalent to increasing the concentration of APDC) resulted in concomitant sample dilution and hence in decreased atomic signals. A compromise was thus made and a sample flow-rate of 1.5 ml/min and an APDC flow rate of 0.3 ml/min were chosen.

The influence of the length of the preconcentration coil, which was located before the activated carbon column in the loop of the injection valve, was investigated over the range 20–550 cm (0.5 mm i.d.). The absorbance difference increased as the tube length increased up to 300 cm, above which it started to decrease. This

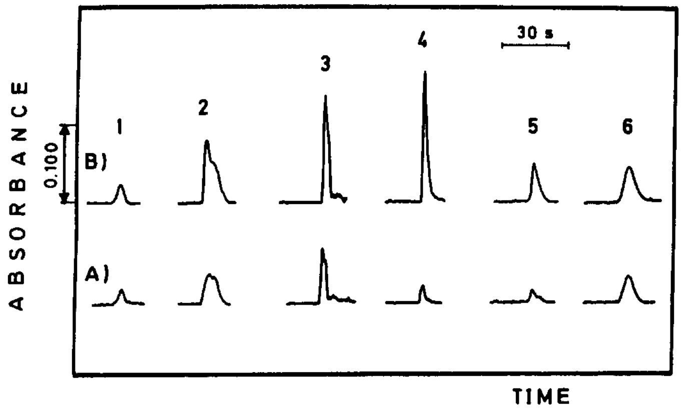

Fig. 2. FIA peaks obtained from different injected eluting solutions. A and B, blank and sample signal, respectively. Sample concentration, 50 ng/ml copper. Peaks: 1 = ethanol or methanol (726; 714); 2 = methyl ethyl ketone (4514; 2343); 3 = 1,2-dichloroethane (3643; 1977); 4 = methyl isobutyl ketone (3707; 534); 5 = 0.5 M $KBrO_3$ in 2*N* nitric acid (1856; 610); 6 = 0.5*M* $K_2Cr_2O_7$ in 2*N* nitric acid (2829; 1697). Peak areas (in μV × s) are given in brackets for sample and blank, respectively. Sample volume, 3.0 ml.

can be ascribed to the fact that lengths shorter than 300 cm (*i.e.* residence times shorter than 20 sec) result in incomplete formation of the chelate; on the other hand, a 300 cm coil gives rise to virtually complete formation and maximum retention. With coils longer than 300 cm, the chelate formed is carried along the system and probably adsorbed on the inner walls of the PTFE tube (*i.e.* spread over a large surface area), so it can not be completely dissolved by the injected MIBK and the signal decreases as the coil length is increased.

Elution

Eight organic and inorganic solvents were assayed as extractants for elution of the adsorbed chelate from the column namely ethanol, methanol, methyl ethyl ketone, 1,2-dichloroethane, methyl isobutyl ketone, *N*,*N*-dimethylformamide, 0.5*M* $KBrO_3$ and 0.5*M* $K_2Cr_2O_7$ (both in 2*N* nitric acid). By using an automated configuration similar to that depicted in Fig. 1, 3.0 ml sample volumes containing 50 ng/ml of Cu(II) in 0.1*N* nitric acid (flow-rate 1.5 ml/min; pumping time, 2 min) and injecting 200 μl of extractant, the above eluting reagents were assayed in order to select the fastest. The results obtained in these experiments are summarized in Fig. 2. The peaks obtained in duplicate experiments with the same extractant were similar; however, solvent changeovers required flushing the column with MIBK in order to remove the remaining adsorbed chelate. As can be seen, the best results (difference between sample and blank) were provided by MIBK, where the chelate was most readily soluble and hence desorbed; in addition the blank signal was lower and no dispersion occurred during transferral to the detector because MIBK is water immiscible. The other extractants provided worse results because they were water miscible and the plug underwent dispersion, or because the elution was incomplete (in both instances, both the peak height and area were smaller). *N*-*N*-dimethylformamide provided no signal difference between sample and blank (similarly to ethanol).

The effect of the MIBK volume was studied between 50 and 300 μl. The adsorbed chelate was eluted throughout this range, but some carry-over was observed below 200 μl. Therefore, 200 μl of MIBK was chosen as optimal as it ensured complete desorption from the column and the signals were very repeatable. Figure 3

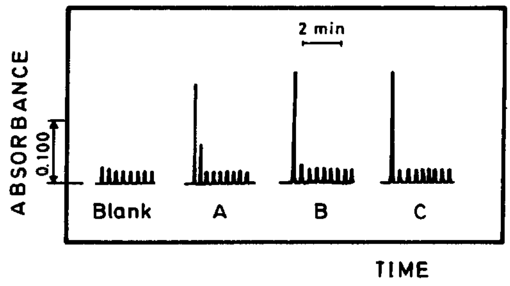

Fig. 3. Absorbance *vs* time plot for the desorption of 50 ng/ml copper solutions obtained by sequential injection of methyl isobutyl ketone. Blank, 0.1*N* nitric acid; A, B and C, 100, 150 and 200–300 μl MIBK. Sample volume, 3.0 ml.

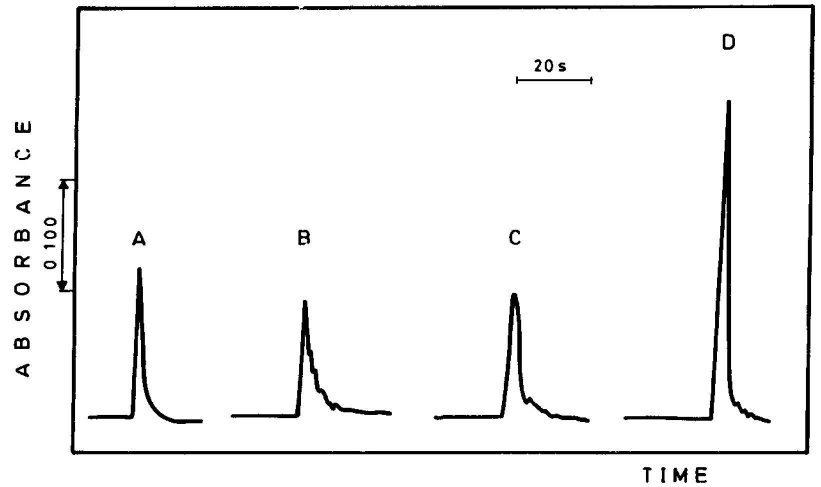

Fig. 4. FIA peaks obtained in the desorption of 150 ng/ml copper solution on different devices. A, 300 cm PTFE coil (0.5 mm i.d.); B, C and D, the same as in A, but supplemented with (B) a planar filter, (C) a cylindrical filter and (D) an activated carbon column. The peak areas (in μV × s) for the sample and blank were: A (2430; 750), B (3260; 560), C (3315; 1150) and D (5010; 550). Sample volume, 1.5 ml.

shows carry-over resulting from injected volumes of 100 μl; it could be eliminated by making a second injection of MIBK at some time (about 15 sec) after the analytical injection, but two peaks would then be obtained per sample. Above 200 μl, a single injection of MIBK was sufficient, so one peak per sample was obtained. The influence of the MIBK flow-rate (water flow-rate) on the peak height was examined in the range 1–6 ml/min. The latter increased with increasing flow-rate up to 3.6 ml/min. Even though the peak height increased, the peak area remained constant throughout. A flow-rate of 4.2 ml/min was thus chosen in order to obtain high peaks and ensure optimal performance of the AAS instrument.

Retention of the chelate on various devices

A comparative study of the chelate retention on an activated carbon column, various filters (with high and low dead volume) and a PTFE coil was carried out with the column or filter placed after the 300 cm preconcentration PTFE coil (coiled 10 mm, 0.5 mm i.d.) in the loop of injection valve. The filters used in this study were of two types and were originally designed for use as cleaning devices in HPLC. The performance of all the devices used in this study (Fig. 4) was compared and the following conclusions can be drawn. (a) With a 300 cm PTFE coil (in the absence of the filter and activated carbon column), the precipitated chelate was adsorbed on the inner walls of the tube, but a fraction of the chelate was probably lost and sent to waste, so the signal decreased and the difference in peak area between sample and blank was the smallest (Fig. 4). (b) No significant changes in the signal resulted from the use of filters after the PTFE coil. In both instances, the precipitated chelate was retained during the preconcentration step and then dissolved with the methyl isobutyl ketone. With planar filter (low dead volume, 100 μl) the signal was higher than with cylindrical filter (high dead volume, 580 μl) because the precipitate was confined in a minimal area, so dissolution was more efficient. (c) The best results were obtained with the activated carbon column, which probably involved two processes: adsorption of soluble and precipitated chelate, which gave rise to a greater difference in peak area between sample and blank. As can be seen in Fig. 4 (D), the peak was sharper, so it enabled use of its height as analytical signal. In summary, while partial precipitation of the chelate took places in the proposed preconcentration flow system, retention was favoured by the activated carbon column, which acted as a mixing filter/adsorption device. Experiments carried out with different lengths of the activated carbon column (between 2 and 4 cm long, 3 mm i.d.) showed 2.5 cm to be the optimal length. The column remained usable for at least 3 months of daily usage.

Figures of merit

Under the optimum chemical conditions, the manifold depicted in Fig. 1 was used to run several calibration graphs for copper(II) by stopping the sample and APDC streams 1, 2 or

Table 1. Characteristic parameters of the calibration graphs and analytical features of the determination of copper with time-based sampling

Time (*min*)	Regression eq., absorbance *vs* *ng/ml*	Linear range (*ng/ml*)	Det. lim. (*ng/ml*)	RSD (%)	Sampling freq. (*hr*)	Preconc. factor
1	$A = -0.002 + 1.9 \times 10^{-3}[Cu^{2+}]$	6–170	1.5	3.5	40	35
2	$A = 0.002 + 3.4 \times 10^{-3}[Cu^{2+}]$	3–95	1.0	2.4	24	65
3	$A = 0.002 + 5.1 \times 10^{-3}[Cu^{2+}]$	2–60	0.6	1.8	17	100

3 min after continuous circulation and using sample volumes of 1.5, 3.0 or 4.5 ml, respectively. Table 1 lists the figures of merit of these graphs and the analytical features of the determination of copper(II) in the range 2–170 ng/ml. The correlation coefficients obtained ranged between 0.996 and 0.998 in all instances. The detection limit was calculated as three-fold the standard deviation of the peak height for 15 determinations of the blank by injecting 200 μl of MIBK in each case. The precision of the method (expressed as the relative standard deviation) was checked on 11 samples containing 10 ng/ml each at different time-based sampling (1–3 min). The precision increased as the sample volume was also increased. Preconcentration factors of up to 100, calculated as the ratio between the slopes of the calibration graphs obtained by this method and by direct aspiration ($A = 0.002 + 0.051$ [Cu^{2+}], copper(II) expressed in μg/ml), were readily achieved.

The effect of many common metal ions which can form complexes with the assayed reagent (APDC) was examined in order to detect potential interferences. The cations investigated included Co^{2+}, Ni^{2+}, Zn^{2+}, Fe^{3+}, Mn^{2+} and Al^{3+} (also present in waters). Such ions as Zn^{2+}, Mn^{2+} and Al^{3+} caused no interference with the determination of 50 ng/ml of copper (time-based sampling, 2 min) at a concentration of 50 μg/ml; neither did 5 μg/ml Fe^{3+}. Higher Fe^{3+} concentrations did interfere (50 μg/ml Fe^{3+} increased the copper signal by about 12%). Also, Co^{2+} and Ni^{2+} interfered at concentrations above 0.5 μg/ml (1μg/ml Co^{2+} or Ni^{2+} decreased the copper signal by about 20%). Some masking agents (citric acid and EDTA) were assayed to diminish the interference of Fe^{3+}, Co^{2+} and Ni^{2+}; the results were not satisfactory, owing to the low pH of the sample (1.0). However, the selectivity achieved enables the determination of copper in waters.

Table 2. Results of the analysis for copper in waters and Recoveries obtained

Sample	Copper found (*ng/ml*)	Recovery* (%)
Tap water 1	6.2 ± 0.3	113
Tap water 2	24 ± 0.1	89
Mineral water 1	1.8 ± 0.1	93
Mineral water 2	1.5 ± 0.1	88
Mineral water 3	1.8 ± 0.1	93
Well water†	583 ± 20	89
Swimming pool water	1.7 ± 0.1	89
River water	2.4 ± 0.1	88

*Averages of five individual determinations by adding 10 ng/ml copper.

†For analysis, the original water sample was diluted 20 times.

Determination of trace amounts of copper in waters

The proposed atomic absorption method was applied to the preconcentration and determination of trace amounts of copper in waters. Prior to this determination, a study of the concentration of iron, cobalt and nickel in these water samples was performed by direct AAS measurements and the metal ions contents of all the water analysed were found to be lower than 0.5 μg/ml (the well water sample was diluted 20-fold); therefore, the proposed method can be applied to the determination of copper in these samples. The results (±standard deviations) obtained in five individual determinations are listed in Table 2. Samples with copper concentrations below 2 ng/ml were analysed by the standard-addition method. The swimming pool water had not been treated with copper sulphate, so the copper concentration was quite low. The results and recoveries obtained by adding 500 ng Cu^{2+} to sample aliquots of 50 ml (10 ng/ml) are also given in Table 2.

CONCLUSIONS

Such a classical collecting material as activated carbon has been shown to present its typical assets of batch work when used in continuous-flow systems. The proposed system is clearly superior to existing continuous-flow alternatives using C_{18} minicolumns.[22,23] Thus, during the preconcentration step, both the sample matrix and the eluent are sent to waste. Also, the preconcentration reactor and the column are located in the loop of the injection valve, so the eluent sweeps any chelate potentially adsorbed by the reactor, thereby avoiding carry-over (in other systems, the eluent is not passed through the preconcentration reactor). Finally, the eluent is water-immiscible and the analyte is not dispersed on transferral to the detector, which rebounds to higher preconcentration factors. The different devices studied showed that the partial precipitation of the chelate favours its complete retention on the activated carbon column.

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