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DETERMINATION OF Mo(VI) IN TAP-WATER AND SEA-WATER BY DIFFERENTIAL-PULSE POLAROGRAPHY AND CO-FLOTATION

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Summary—A new method is described for the microdetermination of Mo(VI) in natural waters and sea-water by differential-pulse polarography based on the catalytic wave caused by Mo(VI) in nitrate medium following preconcentration by co-flotation on Fe(III) hydroxide. In the case of sea-water samples, hexadecyltrimethylammonium bromide (HTAB) was used together with octadecylamine as the surfactant. For the analysis of natural water samples only HTAB is needed. Molybdenum in the range 0.7–5.7 ng/ml has been determined.

It has been shown that the molybdate ion can be reduced polarographically only at pH less than 6.[1,2] Stern[3] found that in acid solutions containing nitrate, a very large wave appeared, owing to a catalytic reduction process involving Mo(VI).[4–7] This wave was used by Lanza *et al.*[8] in a procedure for the determination of molybdenum in steel by differential-pulse polarography (DPP).

Classical polarographic methods have not been used very much for the determination of trace elements in sea-water, because the sensitivity is generally not good enough—stripping voltammetric methods are to be preferred.[9] Prabhu *et al.*[10] have used DPP following preconcentration by co-precipitation.

Co-flotation is a technique which has received a great deal of attention in recent years[11–13] for separating and preconcentrating trace elements from natural waters, waste waters and sea-water. Kim and Zeitlin[14] have determined molybdate in waters by co-flotation with Fe(III) hydroxide, with sodium dodecylsulphate as surfactant, and spectrophotometric measurement. However, the combination of polarography and flotation does not seem to have been used for the determination of trace metals. This approach should be very interesting because the high concentration factor obtained by flotation should make it possible to use the polarographic methods for determination of trace metals levels below the detection limits normally attainable by these techniques. The combination should also allow some interferences to be eliminated.

The probable reason for earlier neglect of this combination of methods is that the surfactants needed in the flotation may suppress not only maxima on polarographic waves, but even the waves themselves.

This paper describes application of the combination for the microdetermination of Mo(VI) in natural waters and sea-water by means of DPP, utilizing the catalytic wave produced by Mo(VI) with nitrate, following preconcentration by co-flotation with Fe(III) hydroxide by means of the surfactants hexadecyltrimethylammonium bromide and octadecylamine.

EXPERIMENTAL

Reagents

All reagents used were of analytical grade, without further purification. The working solutions were prepared weekly by diluting aqueous stock solutions [1000 μg/ml Mo(VI), 0.05*M* Fe(III), 4*M* ammonium nitrate, 0.005*M* hexadecyltrimethylammonium bromide (HTAB), 5*M* nitric acid], and 3-g/l. ethanolic solution of octadecylamine (OA). Solutions of possible interfering ions and of several other surfactants were also prepared. Amberlite IR-120 resin (300–1000 μm) was used as the ion-exchanger.

Apparatus

The polarographic measurements were made with a Metrohm E506 polarograph, E505 stand, EA427 Ag/AgCl reference electrode and EA285 platinum auxiliary electrode. All pH-measurements were made with a Metrohm 654 pH-meter. The flotation device used has been described previously.[15,16]

Procedures

Place 500 ml of the water sample in a 600-ml beaker, and add 1.0 ml of HTAB solution and 1.0 ml of OA solution. In another beaker, precipitate Fe(III) hydroxide by adding 2.0 ml of 2*M* ammonia to 1.0 ml of 0.005*M* Fe(III), and transfer the precipitate to the beaker containing the water sample. Adjust the pH to 4.00 ± 0.1 by careful addition of nitric acid, stirring the mixture for 17 min. Transfer the contents of the beaker quantitatively into the flotation column, already containing 2.0 ml of ethanol, and set the air flow-rate to 32 ml/min, to allow co-flotation to take place. After 5 min interrupt the air flow and discharge the solution in the column (mostly through the side-trap of the column, the remainder by suction through the sintered-glass plate at the bottom of the column. Dissolve the precipitate with 12 ml of 1.25*M* nitric acid then wash the column walls with more nitric acid, and dilute the combined solution and washings to 25 ml with distilled water.

Pass this solution through a 2 × 20 cm column packed with Amberlite IR-120 resin, previously washed with 200 ml of 0.5*M* nitric acid, collecting the effluent in a 50-ml standard flask containing 8.0 g of ammonium nitrate. Elute with 0.5*M* nitric acid, collecting the eluate in the same standard flask until the solution reaches the mark.

Transfer some of the eluate to a polarographic cell, and analyse by DPP, with initial potential 0.0 V, drop-time 0.6 sec, scan-rate −8.3 mV/sec, recorder sensitivity 1.5 mA/mm, mercury column height 57.0 cm, pulse amplitude −50 mV.

Determine the concentration of molybdenum by making standard additions of 1000 ng/ml Mo(VI) solution.

Use the same procedure for natural waters and waste waters of low salinity, but with only HTAB as surfactant.

RESULTS AND DISCUSSION

The catalytic wave in saline medium

A calibration curve was constructed by the method described by Lanza *et al.*,[8] but with a medium containing 35 g of sodium chloride per litre. Under these conditions a well-defined peak with E_p − 0.13 V (Fig. 1) was obtained. The relationship between the Mo(VI) concentration and the intensity of the peak was a linear function of the molybdenum concentration in the range 0.01–10.0 µg/ml.

The effect of several surfactants on the polarographic behaviour was then investigated to find the most suitable from a polarographic point of view: these were then tested in the co-flotation process. The test solutions contained 1 mg of Mo(VI) and 35 g of sodium chloride per litre of 2*M* ammonium nitrate/0.25*M* nitric acid. Increasing quantities of the surfactants HTAB, Triton X-100, Aliquat 336, benzyldimethyltetradecylammonium chloride (zefiramine); sodium oleate, tetramethylammonium bromide and octadecylamine were tried, and changes in peak potential and peak height were noted for DPP and of the half-wave potential for d.c. polarography. The results obtained for peak height are shown in Fig. 2.

The half-wave potential was shifted to more negative values by HTAB concentrations above 125 mg/l. The same effect was observed for more than 12 mg/l. Triton X-100. Zefiramine, sodium oleate and Aliquat 336 produced precipitates in the medium, which caused oscillations of the polarographic current, making measurements difficult. Octadecylamine also caused turbidity in the solution but the polarographic determination was not affected until the surfactant concentration exceeded 120 mg/l. Such observations, and the results given in Fig. 2, indicated that HTAB would be the most convenient surfactant because it did not affect the polarography and was excellent in the co-flotation process for solutions of low salinity.[10] In solutions of high salinity, it proved necessary to add octadecylamine as well.

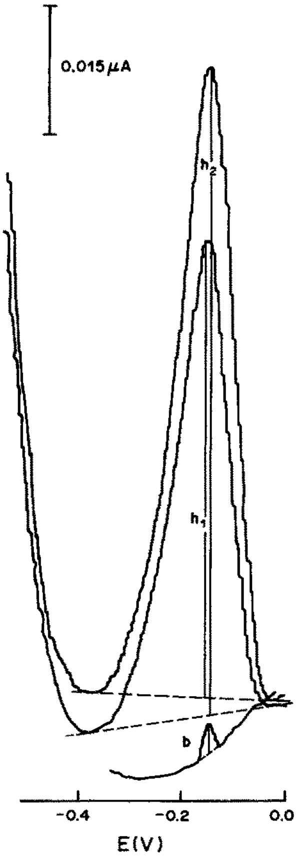

Fig. 1. DPP peak corresponding to a sea-water sample (h_1, unspiked sample; h_2, sample spiked with 2.0 ng/ml Mo; b blank).

Next, a systematic study was made of possible interferences in presence of HTAB. Different cationic and anionic species were selected either because they could form complexes with Mo(VI) or because they are normally present in natural waters or sea-water.

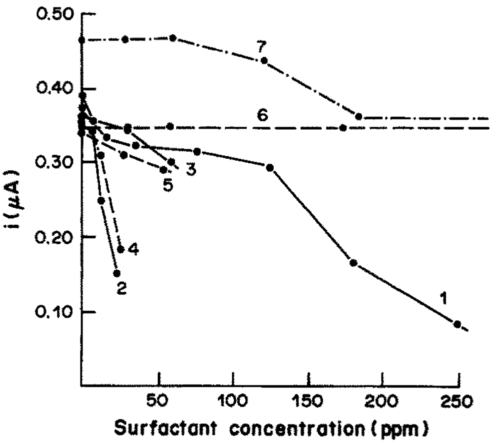

Fig. 2. Variation in DPP peak intensity for Mo(VI) determination, as a function of the nature and quantity of surfactant added (1, HTAB; 2, Triton X-100; 3, Aliquat 336; 4, zefiramine; 5, sodium oleate; 6, tetramethylammonium bromide; 7, octadecylamine).

Table 1. Study of interferences in the polarographic determination of molybdenum (interference positive if an error exceeding ±3% is observed)

Species	Interference	Concentration ratio, ion:Mo(VI)
Cu(II)	+	>0.5:1
Pb(II)	−	100:1
Cd(II)	−	100:1
Zn(II)	−	100:1
Ni(II)	−	100:1
Co(II)	−	100:1
Hg(II)	−	100:1
Mn(II)	+	>0.5:1
Mg(II)	+	>1:1
Fe(III)	+	>100:1
Cr(VI)	−	100:1
bromide	−	1000:1
iodide	+	>5:1
nitrite	−	100:1
phosphate	−	1500:1
oxalate	−	100:1
tartrate	−	100:1

The results are shown in Table 1. In each case the concentration range studied was determined by the interferent:analyte ratio usually found in sea-water. Cu(II), Mn(II), Mg^{2+} and iodide interfered seriously. Fe(III) caused an appreciable reduction in peak height when present at $\geqslant 100$-fold ratio to Mo(VI) but it was still possible to measure the Mo(VI) quantitatively by the standard-additions method, up to an Fe(III):Mo(VI) ratio of 200:1. These interferences and the sensitivity levels achieved made it evident that the polarographic method could not be used directly for sea-water, and that a preconcentration would be essential to improve the sensitivity and eliminate the interferences.

Co-flotation

The preconcentration step was optimized in two stages. In the first, synthetic samples containing 5 mg/l. Mo(VI) were used because it was then easier to monitor the kinetics and the yield of the process by measurement of the residual Mo(VI) in the bulk solution at different times during the co-flotation. Once optimum conditions had been found in this way, the second stage was commenced, in which the co-floated molybdenum was determined polarographically, its initial concentration being progressively reduced until ng/ml levels were reached. The optimum conditions obtained in the first stage served only as a guide in the second stage, because the Mo(VI):co-precipitant and Mo(VI):surfactant ratios were very different in the two series of experiments.

Natural and low-salinity waters

HTAB was used as the surfactant and Fe(III) hydroxide as the co-precipitant (because this was the most commonly used co-precipitant in co-flotation procedures[16,17] and is convenient because its colour can be used for monitoring the flotation). An initial pH of 4.0 was used for the co-flotation, to eliminate most interferences. [The optimum pH-range for co-flotation of Cu(II) with Fe(III) hydroxide is >7,[18] and Mn(II) is floated as the hydroxide by dodecylsulphate[19] at pH 11.5; neither Mn(II) nor iodide seems to be floated at this pH.[20,21]] Moreover, colloidal Fe(III) hydroxide has maximum positive charge at this pH and is capable of quantitatively adsorbing the anionic Mo(VI) present in solution, at pH > 1.0.[17]

The experimental conditions were optimized by means of the simplex program COFLOT.[22] The air flow-rate, co-precipitant and surfactant concentrations, pH and induction time were the variables. Table 2 gives the initial simplex for this investigation. For samples containing Mo(VI) at the μg/ml level the optimum set of values, obtained after 21 experiments, was air flow-rate 32 ml/min, co-precipitant 2.26 ml of $0.05M$ Fe(III), surfactant 2.46 ml of $0.005M$ BHTA, pH 3.75, induction time 17 min.

Further experiments were then performed for fine adjustment of the operating conditions, starting with those provided by COFLOT, and confirmed the optimal ranges yielded by the program. These experiments also showed that the co-flotation was initially faster when the gas flow in the column was increased, as shown in Table 3, but the foam consistency became poorer as the air flow-rate increased, causing the precipitate to settle back into the solution. The conditions found by using COFLOT were indeed optimal, but not all critical; 30% variation of the amount of surfactant or co-precipitant or in the induction produced no appreciable difference in the co-flotation yield, but the pH-value had to be strictly controlled within the range 4.0 ± 0.1 for reproducible results to be obtained.

Under these conditions triplicate experiments gave yields of 93.0, 92.9 and 93.6%. The best results were obtained by co-flotation at 17 ± 3°. As already stated,

Table 2. Initial simplex for optimization of Mo(VI) co-flotation in low-salinity waters

Vertex	Air flow-rate *ml/min*	Co-precipitant, *ml*	Surfactant (HTABr), *ml*	pH	Induction time, *min*	Mo(VI) recovery, %
1	100	1.0	3.0	4.0	10	83.0
2	45	1.0	3.0	4.0	10	90.9
3	100	2.0	3.0	4.0	10	91.3
4	100	1.0	2.0	4.0	10	84.0
5	100	1.0	3.0	9.0	10	13.6
6	100	1.0	3.0	4.0	5	84.2

Table 3. Effect of the gas flow-rate in the column on the kinetics of Mo(VI) co-flotation [recovery of Mo(VI) as a function of the time elapsed in the co-flotation process]

Flow, *ml/min*	Time, *min*				
	0.5	1.0	5.0	10.0	15.0
32.0	31.6	86.0	92.0	92.0	93.0
60.0	29.4	72.0	90.5	90.5	90.5
80.0	76.0	90.4	92.0	92.0	92.0
100.0	77.7	86.7	89.2	90.0	90.0

after the co-flotation only the presence of iron causes problems with the Mo(VI) determination. Other impurities in the regents do not produce peaks in the working potential range, and the typical blank value of 0.25 ng/ml is satisfactory.

Obviously the use of thorium or aluminium hydroxides as co-precipitant should eliminate the interference experienced with iron(III) in the DDP technique. However, use of thorium hydroxide as co-precipitant showed a significant lack of reproducibility, the average recoveries of Mo(VI) ranging around 70%. Use of aluminium hydroxide was even worse, only 20% of the Mo(VI) being recovered at best.

Saline waters

When the experimental conditions given above for low-salinity samples were used to preconcentrate molybdenum from high-salinity samples, 10.4% of the Mo(VI) added was recovered. We have reported previously on the inability of HTAB–metal hydroxide systems to separate trace metals by co-flotation from media with salinity similar to that of sea-water.

For such samples, the HTAB–OA combination (based on previous results)[23] proved to be the best for the co-flotation. Octadecylamine has low solubility in aqueous media, so to get good recovery in the co-flotation it was necessary to use it at the lowest concentration that was still efficient. It was found that 12 mg/l. octadecylamine in the bulk solution and a concentration of HTAB similar to that used for non-saline media gave good separation without difficulty. A higher concentration of OA in the samples did not improve the co-flotation yield and interfered in the final DPP analysis.

Table 4. Results for analysis of synthetic samples

No.	Sample*	Mo(VI) added, *ng/ml*	Mo(VI) found, *ng/ml*	Recovery, %
1	LS	1.00	0.86	86
2	LS	1.00	1.00	100
3	LS	1.00	0.93	93
4	LS	1.00	0.82	82
5	LS	1.00	0.98	98
6	LS	1.00	1.20	120
7	LS	1.00	0.98	98
8	HS	2.00	1.92	96
9	HS	2.00	2.00	100
10	HS	2.00	1.75	87.5
11	HS	2.00	1.92	96
12	HS	2.00	1.78	89
13	HS	2.00	1.77	88.5
14	HS	2.00	2.06	103

*LS = low salinity sample (distilled water); HS = high salinity sample (synthetic sea-water).

A series of optimization experiments showed that the best results are obtained under conditions similar to those previously established for non-saline waters, so those conditions (plus addition of 12 mg of octadecylamine per litre) were adopted for subsequent fine-tuning optimization.

Sublate analysis

In the second stage of the optimization process, polarographic analysis was used to determine the co-flotation yield after 5 min of flotation. Synthetic saline and non-saline samples with Mo(VI) contents of 100 and 10 ng/ml were tested. With decreasing Mo(VI) concentration, the results became less satisfactory because the polarographic wave was seriously affected by the high levels of surfactant species and co-precipitant. Also, the pH-value initially selected (3.75) then caused rather poor reproducibility. A flotation pH of 4.0 and use of lower quantities of surfactant and co-precipitant were found to provide less critical conditions for the precipitation, and satisfactory results were obtained. Even under these conditions, however, Mo(VI) concentrations of 1 ng/ml could not be determined properly, because the high Fe(III):Mo(VI) ratio of 2800 seriously affected the polarographic signal. The Fe(III) and Mo(VI) were therefore separated by ion-exchange, and the conditions given in the experimental section were established as optimal for samples with low concentrations of Mo(VI) (1–100 ng/ml). The results obtained under these conditions for the analysis of synthetic samples are shown in Table 4.

Determination of Mo(VI) in real samples

Once suitable experimental conditions had been found for the determination of trace levels of Mo(VI), samples of tap-water and sea-water were analysed. The results are shown in Table 5. Good reproducibility was obtained, with average values of 0.7 ng/ml for the tap-water samples and 5.7 ng/ml for the sea-water.

Table 5. Results for analysis of two real samples

No.	Sample type*	Mo(VI) found, *ng/ml*
1	TW	0.72
2	TW	0.67
3	TW	0.70
4	SW	5.5
5	SW	5.8
6	SW	5.8

*TW = tap-water; SW = sea-water samples taken from Cádiz Bay.

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