



ELSEVIER

Journal of Chromatography A, 673 (1994) 291–294

JOURNAL OF  
CHROMATOGRAPHY A

Short Communication

Simultaneous determination of cobalt and nickel by reversed-phase high-performance liquid chromatography with diethyldithiocarbamic acid<sup>☆</sup>

V. González Rodríguez, J.M. Castro Romero\*, J.M. Fernández Solís,  
J. Pérez Iglesias, H.M. Seco Lago

*Department of Analytical Chemistry, University School Polytechnic of Ferrol, University of La Coruña, 15405 Ferrol, Spain*

(First received December 6th, 1993; revised manuscript received February 27th, 1994)

**Abstract**

The reagent diethyldithiocarbamic acid has been examined for the high-performance liquid chromatographic separation of cobalt(II) and nickel(II) chelates on reversed-phase HPLC columns (150 × 3.9 mm) packed with Nova-Pak C<sub>18</sub>, 4 μm. The metal-diethyldithiocarbamic chelates were preconcentrated by solvent extraction. An aliquot of sample containing copper, cobalt and nickel in a mixture was transferred to a well-stoppered test tube to which was added reagent [diethyldithiocarbamic acid 0.5% in ethanol–water (1:1), pH 10] and 10 ml organic solvent (diethyl ether). After shaking with mechanical shaker for 5 min, the organic layer was separated and 0.1 ml transferred to another tube containing methanol (1 ml). The methanolic solution (15 μl) was injected, on the reversed-phase HPLC column. The complexes are eluted with methanol–water (75:25) at a flow-rate of 0.5 ml min<sup>-1</sup>. The detection is carried out with a UV detector at 260 nm. The method shows several advantages: short analysis time, minimized sample preparation, minimized effect of interfering ions, a low detection limit (50 ppb for nickel and 5 ppb for cobalt) and good reproducibility, making it suitable for many types of samples, including alloys.

**1. Introduction**

The analysis of single or multiple metal ions in trace amounts in environmental matrices is a general problem. As a result many methods for the preconcentration of metal ions have been described [1,2]. Of these, solvent extraction has been, until recently, the most popular method.

Liquid–liquid extraction is a simple and convenient approach in separation science and it is one of the most frequently used sample pre-treatment techniques in the determination of trace metals. In previous steps complexes of metal ions can be obtained, to increase the sensitivity [3]. Diethyldithiocarbamic acid is a widely used organic chelating reagent. Most of the chelates formed by this reagent are coloured and can be extracted into a variety of organic solvents.

A wide variety of techniques have been described for the determination of metal chelates. Spectroscopic methods are by far the most popu-

\* Corresponding author.

<sup>☆</sup> Presented at the 22nd Annual Meeting of the Spanish Chromatography Group, Barcelona, October 20–22, 1993.

lar but this traditional method requires that the complexing agent is available in highly pure form and of sufficiently high solubility in the liquid medium used in the investigation. In addition, the absorption wavelengths of the ligand and complex will be very difficult to measure accurately. Liquid chromatography may be able to make up for this deficiency. These complexes of metal ions can be separated by high-performance liquid chromatography (HPLC) [4–7]. Khuhawar and Soomro [5] have examined the reagent bis(acetylpyvalylmethane)ethylenediimine for the HPLC separation of metal chelates with UV detection. A HPLC technique for the determination of metals as their 8-hydroxyquinolate complexes using spectrophotometric detection at 400 nm is described by Ryan and Meaney [6].

Presently the application of reversed-phase (RP) HPLC to the determination of metal chelates is a promising alternative approach for overcoming the lack of selectivity of the chelating reagents. HPLC has attractive advantages such as high sensitivity, selectivity and simultaneous detection capability.

In this paper, a new simultaneous determination of cobalt(II) and nickel(II) by RP-HPLC is described, with previous solvent extraction with diethyl ether and diethyldithiocarbamic acid as reagent. Separation of chelates and ligand was carried out by RP-HPLC using UV detection.

## 2. Experimental

### 2.1. Chromatographic instrumentation

The liquid chromatographic system consisted of a Waters Model 501 pump, a Waters 486 UV-Vis spectrophotometric detector, a Waters Model U6K universal liquid chromatograph injector, and a Waters 746 data module integrator. The column used was a Waters Nova-Pak C<sub>18</sub> (150 × 3.9 mm) filled with dimethyloctadecylsilyl-bonded amorphous silica (particle size 4 μm).

### 2.2. Materials

All the chemicals used were of analytical-reagent grade. Methanol was supplied by Merck. The water was purified using a Milli-Q system (Millipore). Analytical-reagent grade sodium diethyldithiocarbamate (trihydrate) (Merck) was used. All metal salt solutions were prepared by dilution of the 1000 ppm stock standard solutions (Merck atomic absorption grade).

### 2.3. Sample preparation

An aliquot of sample containing cobalt and nickel in a mixture was transferred to a well-stoppered test tube to which was added reagent [diethyldithiocarbamic acid 0.5% in ethanol-water (1:1), pH 10] and 10 ml organic solvent (diethyl ether). After shaking with a mechanical shaker for 5 min, the organic layer was separated and 0.1 ml transferred to another tube containing methanol (1 ml).

### 2.4. Chromatographic procedures

The eluent used was methanol-water (75:25). The flow-rate of the eluent was 0.5 ml min<sup>-1</sup> (3000 p.s.i.; 1 p.s.i. = 6894.76 Pa). It was monitored at 260 nm. The methanolic solution of the sample (15 μl) was injected on the RP-HPLC column.

## 3. Results and discussion

### 3.1. Chromatographic separation

Among the metal ions tested, the diethyldithiocarbamic chelates of cobalt(II) and nickel(II) yielded good peaks on the chromatogram, as shown in Fig. 1. Complete separation between chelate reagent and the two chelates was obtained. The Ni(II) chelate is eluted first and the cobalt(II) chelate is eluted second.

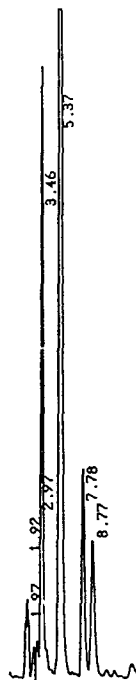


Fig. 1. HPLC separation of diethyldithiocarbamic acid chelates of Ni(II) (1 ppm) and Co(II) (0.1 ppm). Column, Nova-Pak C<sub>18</sub> (150 × 3.9 mm); eluent, methanol–water (75:25); flow-rate 0.5 ml min<sup>-1</sup>; detection wavelength, 260 nm; injection volume, 15 μl. Peaks: solvent (*t<sub>R</sub>* 3.46 min); reagent (5.37 min); Ni(II) (7.78 min); Co(II) (8.77 min).

The effects of variation in chelate reagent concentration, pH, temperature, interferences and the reproducibility were investigated for the extraction of 0.1 ppm of cobalt and 1 ppm of nickel.

### 3.2. Influence of diethyldithiocarbamic acid concentration

The influence of diethyldithiocarbamic acid concentration on the chelates is shown in Fig. 2. To form the chelate are necessary 2 ml of chelating reagent. This amount allows an extraction of cobalt(II) and nickel(II) quantitatively and reproducibly. The composition of the chelates was 1:2 (metal:ligand).

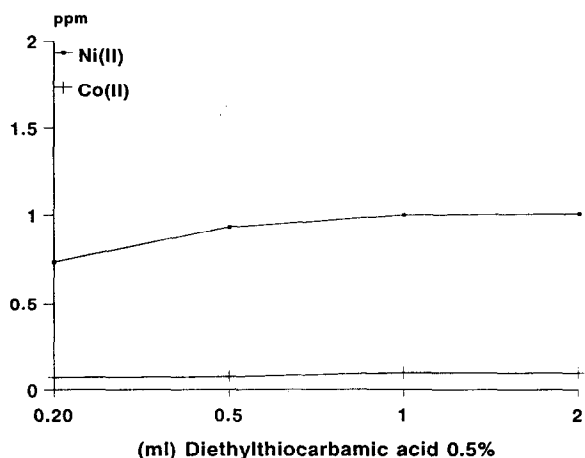


Fig. 2. Influence of diethyldithiocarbamic acid concentration on the extraction of chelates. Other conditions as in Fig. 1.

### 3.3. Influence of the pH, temperature and stability

The extraction capacity of the chelate were investigated in the pH range 1.6–10.2. Chelates of cobalt(II) and nickel(II) in acidic or in basic solution are extracted in a similar way. But the peak of nickel(II) chelates showed irregular interferences in the pH range 1.5–6.0. For analytical purposes the optimum working range is pH 6.5–10.

With increasing temperature the amount of detected metal ions decreases, mainly nickel(II) chelates (Fig. 3).

The detector response to freshly prepared and “aged” standard solutions of the metal chelates was similar for periods up to 4 h. Concentration values for cobalt(II) and nickel(II) chelates remained constant.

### 3.4. Calibration and detection limits; reproducibility

A linear calibration was obtained from injections of 0.01–1 ppm for cobalt(II) and 0.1–5 ppm for nickel(II):

$$\text{Ni(II)}: y = 2.0 \cdot 10^5 x - 1.5 \cdot 10^4; r = 0.9997$$

Table 1  
Reproducibility

	Ni(II) (1 ppm)	Co(II) (0.1 ppm)	Ni(II) (5 ppm)	Co(II) (0.5 ppm)
	198848	152205	996782	882115
	191879	151169	988993	955453
	207724	157520	1164932	924668
	187730	158266	1046346	924550
	195130	148623	1148486	961243
	177638	142858	1072428	923219
	187531	149359	1082664	927743
Mean	198354	151429	1071519	928427
R.S.D. (%)	5.0	3.5	6.4	2.7

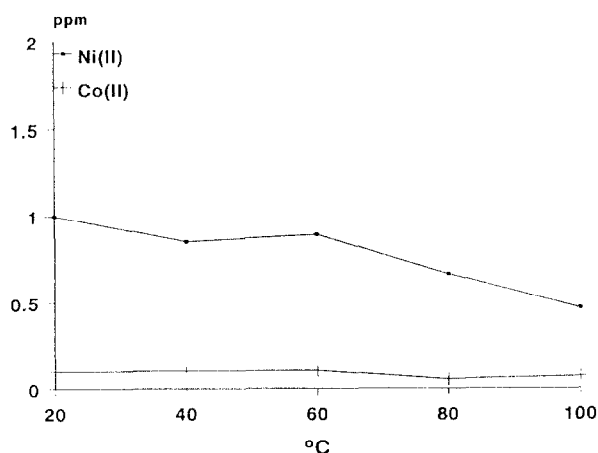


Fig. 3. Influence of temperature on the extraction of chelates. Other conditions as in Fig. 1.

$$\text{Co(II)}: y = 1.5 \cdot 10^6 x - 7.5 \cdot 10^3; r = 0.9999$$

The detection limits (signal-to-noise ratio 3) were 5 ppb for cobalt(II) and 50 ppb for nickel(II).

These values demonstrate the reproducibility of the method. Data are shown in Table 1.

### 3.5. Interferences

The effect of foreign species on the determination of Co(II) and Ni(II) was studied. A level of 10 ppm of Zn(II), Cd(II), Mg(II), Mn(II), Li(I), Hg(II) and Na(I) is tolerated in the determination. However, the determination of Co(II) and Ni(II) is interfered by a level of 10

ppm of Se(IV), Ba(II), Be(II), Ca(II), Sr(II), K(I) and Ag(I).

### 4. Conclusions

Trace enrichment of metal ions using solvent extraction is an effective tool for the enhancement of sensitivity and selectivity when applied to the analysis of trace metals as their diethyldithiocarbamate complexes.

The method shows several advantages: short analysis time, simultaneous determination minimizes analysis time, and it decreases the time spent in sample preparation, minimized effect of interfering ions, and a good reproducibility.

### References

- [1] M. Valcárcel and A. Gómez (Editors), *Técnicas Analíticas de Separación*, Reverté, Barcelona, 1988, pp. 1–51.
- [2] J.P. Brunette and M.J.F. Leroy, *Analisis Mag.*, 20 (1992) M30.
- [3] F. Bermejo, in H.A. Flaschka and A.J. Barnard (Editors), *Chelates in Analytical Chemistry*, Vol. 5, Marcel Dekker, New York, 1976, pp 1–33.
- [4] G. Bazylak and J. Maslowska, *Analisis*, 20 (1992) 611.
- [5] M.Y. Khuhawar and A.I. Soomro, *Talanta*, 39 (1992) 609.
- [6] E. Ryan and M. Meaney, *Analyst*, 117 (1992) 1435.
- [7] N. Uehara, K. Morimoto and Y. Shijo, *Analyst*, 117 (1992) 977.