Detection Limit of Ni(II)bis[di(2,2,2-trifluoroethyl)dithiocarbamate] Determined by Gas Chromatography with Electron Capture Detector

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Capillary gas chromatography with electron capture detector was used for the determination of a detection limit of Ni(II)bis[di(2,2,2-trifluoroethyl)dithiocarbamate] ($Ni(TFDEDTC)_2$) in hexane solutions. The given chelate was prepared by the reaction of Ni ions in aqueous samples with sodium(2,2,2-trifluoroethyl)dithiocarbamate and extracted to hexane. Under given chromatographic conditions 10 pg of $Ni(TFDEDTC)_2$ was detected with a relatively high reliability at signal to noise ratio $S/N = 3$.

Sodium(2,2,2-trifluoroethyl)dithiocarbamate (Na(TFDEDTC)) is a suitable reagent for the gas chromatographic determination of some divalent and trivalent metals [1]. With Ni(II) it produces $Ni(TFDEDTC)_2$ chelate which is thermally stable up to 260 °C and at these temperatures exhibits relatively high vapour pressure. Gas chromatographic (GC) determination of Ni in aqueous samples thus consists of several steps: i) preparation of $Ni(TFDEDTC)_2$ by addition of Na(TFDEDTC) into the aqueous sample, ii) extraction of $Ni(TFDEDTC)_2$ with a proper solvent, and iii) analysis of the obtained $Ni(TFDEDTC)_2$ solution with packed or capillary GC technique with various types of detectors [1].

$Ni(TFDEDTC)_2$ can be determined by GC with flame ionization detector (FID) in the nanogram range. The calibration curve of $Ni(TFDEDTC)_2$ is linear with FID when separating 50—10000 ng of $Ni(TFDEDTC)_2$. When using electron capture detector (ECD) picograms can be detected after separating $Ni(TFDEDTC)_2$ in a packed column [2]. Analysis of $Ni(TFDEDTC)_2$ by combination of mass spectrometry with gas chromatography (GC-MS) allows to determine nanograms of Ni in biological fluid [3]. Results obtained by analysis of $Ni(TFDEDTC)_2$ in spiked model samples with GC-MS using a nonpolar capillary column correspond to those obtained with atomic absorption spectrometry (AAS) (4.14 $\mu g\ g^{-1}$ found by GC-MS and 4.35 $\mu g\ g^{-1}$ by AAS) [3]. It has been shown that the calibration curve of $Ni(TFDEDTC)_2$ found by capillary GC with nonpolar stationary phases is linear in the range of 2—1200 ng for FID and 50—1200 pg for ECD [4]. As this method contains also preconcentration steps (extraction of $Ni(TFDEDTC)_2$ into solvent and focusing of separated zones in retention-gap during GC analysis) it allows to detect ppb levels with FID and ppt levels with ECD of Ni in aqueous solutions [4]. Calibration curve of $Ni(TFDEDTC)_2$ found by GC on moderately polar capillary column (OV-1701) was, however, not linear even in the nanogram range [4]. GC-MS analysis in selected ion monitoring (SIM) mode allowed to detect 50 ng of $Ni(TFDEDTC)_2$ which gave the possibility to analyze $\mu g\ dm^{-3}$ of Ni in urine samples [5]. The different detection limits for capillary GC analysis of $Ni(TFDEDTC)_2$ were found for ECD (0.5×10^{-12} g) and a thermoionization detector selective for nitrogen (NPD) and flame photometric (FPD) detection techniques ($d(N) = 1.2 \times 10^{-12}\ g\ s^{-1}$ for NPD and $d(S) = 0.9 \times 10^{-10}\ g\ s^{-1}$ for FPD) [6]. It has been moreover found that the recovery of $Ni(TFDEDTC)_2$ from water and its analysis by capillary GC depends on the nature of extraction agent [7]. Hexane was found as the best solvent for extraction of $Ni(TFDEDTC)_2$ from aqueous solutions (recovery 100 %) while the recovery using aromatic solvents depended on the quality of solvent [7].

The aim of this paper is to show the detection limit of $Ni(TFDEDTC)_2$ determined by capillary GC with ECD detection technique.

EXPERIMENTAL

Solvents used were as follows: hexane, pure (Slovnaft, Bratislava, Slovakia) purified using the procedure described in [8], benzene (anal. grade, Lachema, Brno, Czech Republic).

All chemicals were destined for synthesis (Lache-

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ma, Brno, Czech Republic). Lindane was delivered by Aldrich (ALDRICH-CHEMIE, Steinheim, Germany).

An HP 5890 series II gas chromatograph equipped with cold on-column injector (both with silicone septum and duck-bill), flame ionization detector (FID), ^{63}Ni electron capture detector (ECD), programmable inlet pressure and injector temperature was used. Hydrogen (99.996 %) was used as a carrier gas. Nitrogen (99.999 %) with the flow rate 60 cm^3 min^{-1} was used as make-up gas for ECD. For FID 30 cm^3 min^{-1} of hydrogen (99.99 %), 40 cm^3 min^{-1} of nitrogen (99.99 %) (make-up gas), and 400 cm^3 min^{-1} of air were used. All gases were purchased from Linde, Bratislava, Slovakia.

A 3396 Integrator Series II and ChemStation 3365 software (Hewlett—Packard, Avondale, USA) were used for recording and evaluating chromatograms.

For GC analyses of $Ni(TFDEDTC)_2$ following fused silica capillary columns were used:

Column HP-5, 13.5 m long capillary with 0.53 mm i.d. coated with 2.65 μm film thickness of 5 % poly(dimethylsiloxane-*co*-methylphenylsiloxane) (Hewlett—Packard, Avondale, USA);

Column SPB-1, 17 m long capillary with 0.25 mm i.d. coated with 1 μm film thickness of poly(dimethylsiloxane) (Supelco, Bellefonte, USA).

Three different modes of working conditions were used for analysis of $Ni(TFDEDTC)_2$ with GC:

Mode *A*: Carrier gas initial inlet pressure 20 kPa (rel.) was increased after 2 min to 200 kPa (rel.) with the rate of 200 kPa (rel.) min^{-1} Column and injection temperatures were increased from 50 °C (2 min) with a rate of 40 °C min^{-1} to 120 °C, then with a rate of 2 °C min^{-1} to 200 °C and with a rate of 40 °C min^{-1} to 260 °C. Temperature of both FID and ECD was 280 °C.

Mode *B*: Carrier gas constant inlet pressure (20 kPa (rel.)). Column and injection temperatures were increased from 50 °C with a rate of 40 °C min^{-1} to 170 °C and with a rate of 3 °C min^{-1} to 240 °C. Temperature of ECD was 280 °C.

Mode *C*: Carrier gas constant inlet pressure (20 kPa (rel.)). Column temperature increased from 50 °C (1 min) with a rate of 40 °C min^{-1} to 200 °C (2 min) and with a rate of 5 °C min^{-1} to 230 °C. Injector temperature increased from 50 °C with gradient 600 °C min^{-1} to 230 °C where it was kept isothermal. Temperature of ECD was 280 °C.

$Ni(TFDEDTC)_2$ chelate was prepared by mixing equal volumes of 0.02 mol dm^{-3} aqueous solution of $NiCl_2$ and 0.04 mol dm^{-3} aqueous solution of Na(TFDEDTC) according to the already published procedure [9] and its purity was checked with elemental analysis using an Elemental Analyzer EA-1108 (C. Erba, Milan).

As the Na(TFDEDTC) was not commercially available, it was synthesized using already published procedures [l]. Ethyl trifluoroacetate was prepared from sodium trifluoroacetate and ethanol [10] in an 80 % yield, 2,2,2-trifluoroacetamide by reaction of ethyl ester of trifluoroacetic acid with gaseous ammonia [11] in a 99 % yield, 2,2,2-trifluoroethylammonium chloride from 2,2,2-trifluoroacetamide [12] in a yield of 80 %, *N*-(2,2,2-trifluoroethyl)-2,2,2-trifluoroacetamide from 2,2,2-trifluoroethylammonium chloride and 2,2,2-trifluoroacetamide in a 98 % yield [13], bis(2,2,2-trifluoroethyl)amine from *N*-(2,2,2-trifluoroethyl)-2,2,

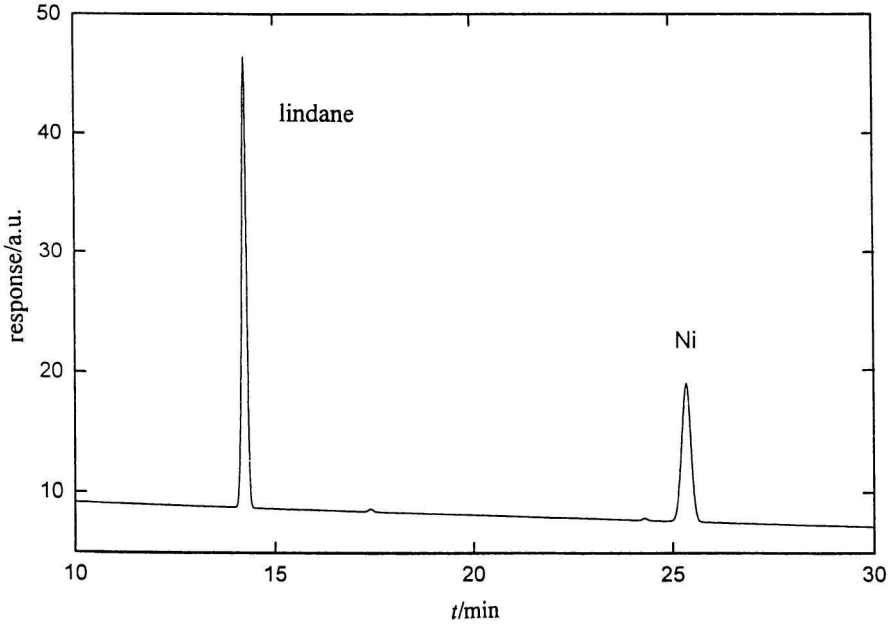

Fig. 1. GC separation of a hexane solution of lindane and $Ni(TFDEDTC)_2$ model sample on column SPB-1 detected with FID. Mode *A* working conditions.

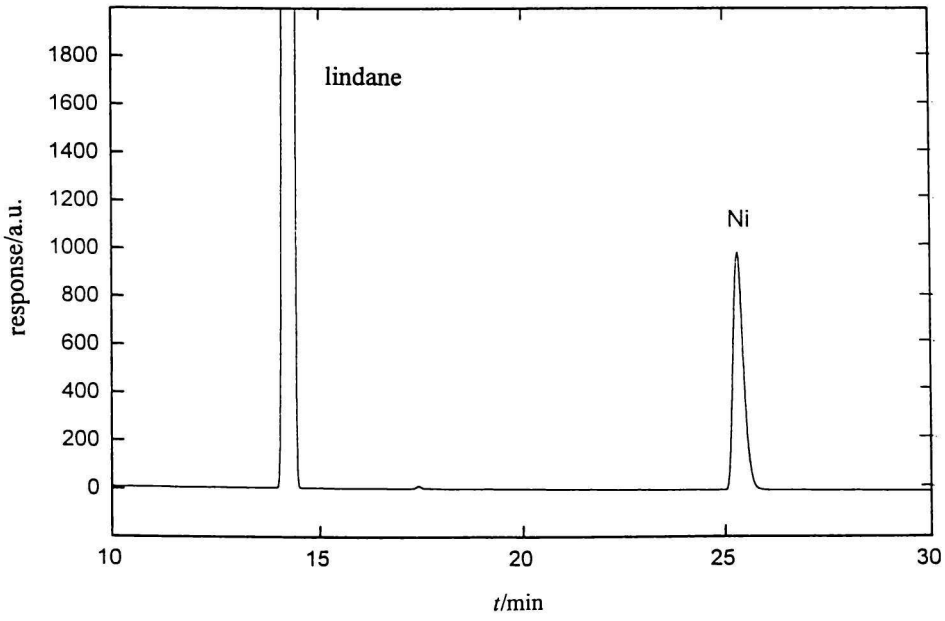

Fig. 2. GC separation of a hexane solution of lindane and Ni(TFDEDTC)$_2$ model sample on column SPB-1 detected with ECD. Mode *A* working conditions.

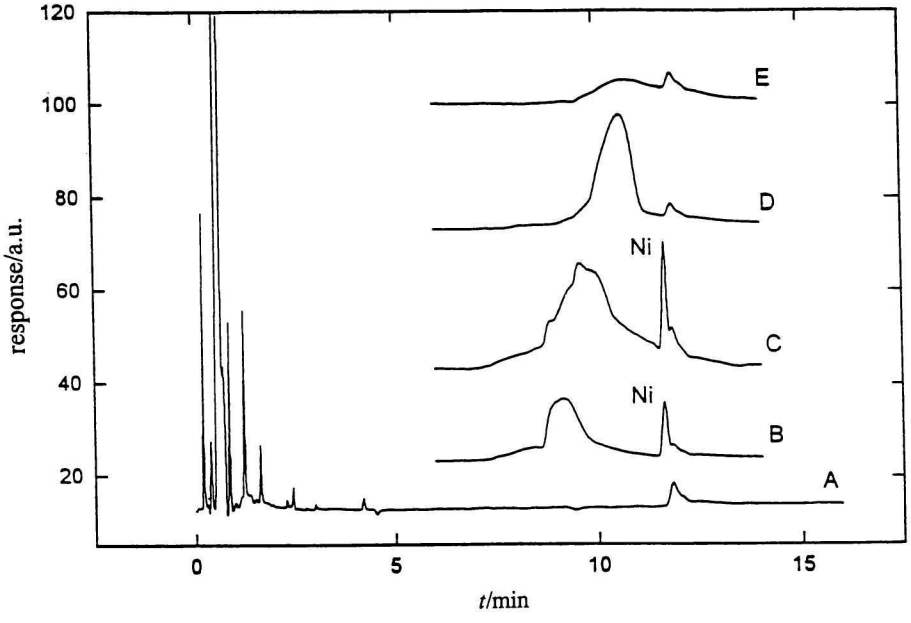

Fig. 3. Chromatograms obtained by GC-ECD analyses of 1 mm^3 of benzene (A) and 1 mm^3 of solution of Ni(TFDEDTC)$_2$ in benzene (2 ng mm^{-3}) in dependence of time elapsed from the preparation of this solution after 30 min (B), 60 min (C), 90 min (D), and 120 min (E) on column HP-5. Mode *B* working conditions.

2-trifluoroacetamide in a 78 % yield [13], sodium salt of di(2,2,2-trifluoroethyl)dithiocarbamic acid Na(TFDEDTC) according to [14].

RESULTS AND DISCUSSION

From the results published in literature it follows that for the gas chromatographic determination of Ni(TFDEDTC)$_2$ both FID and ECD can be applied. Lindane is often used as an internal standard. GC separation of a hexane model mixture of lindane and Ni(TFDEDTC)$_2$ on capillary column SPB-1 detected with FID and ECD is shown in Figs. 1 and 2, respectively.

Evaluation of obtained chromatograms shows that for the injection of equal amount of Ni(TFDEDTC)$_2$ the response of ECD is 75 times higher (Fig. 2) than the response of FID (Fig. 1). No changes were ob-

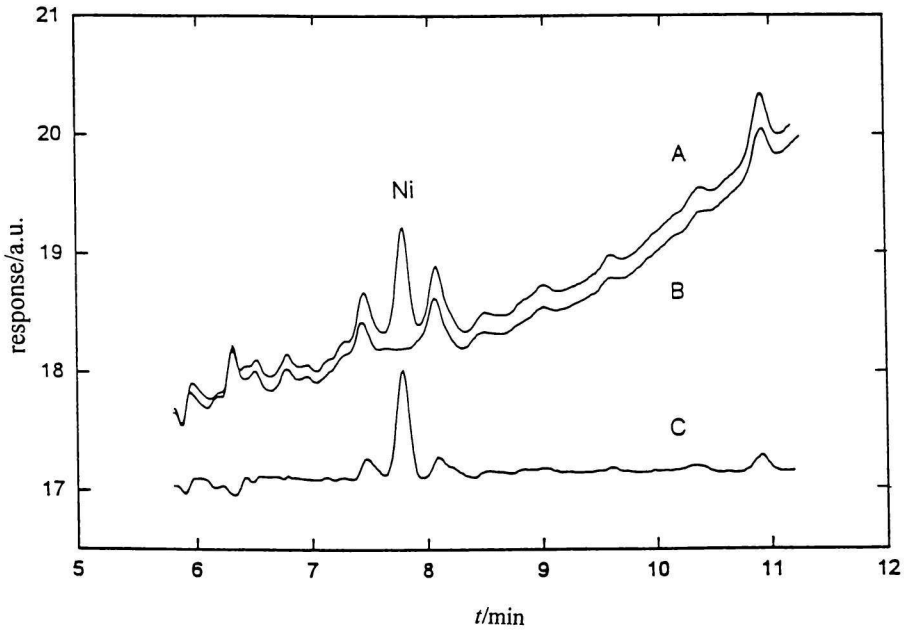

Fig. 4. Chromatograms obtained by GC-ECD analyses of 10 pg of $Ni(TFDEDTC)_2$ dissolved in 1 mm^3 of purified hexane (A), of 1 mm^3 of purified hexane (B), and subtraction of both chromatograms (A − B = C). Separation was performed in HP-5 capillary using Mode *C* working conditions.

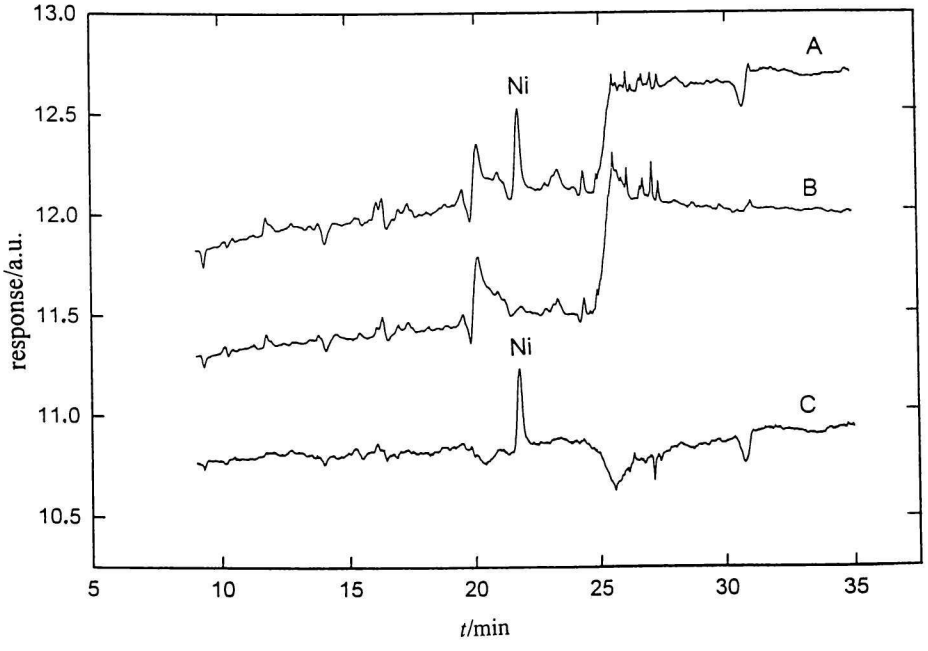

Fig. 5. Chromatograms obtained by GC-ECD analyses of 10 pg of $Ni(TFDEDTC)_2$ dissolved in 1 mm^3 of purified hexane (A), of 1 mm^3 of purified hexane (B), and subtraction of both chromatograms (A − B = C). Subtraction of chromatograms was performed using software built in HP 3365 ChemStation (see Experimental). Separation was performed in SPB-1 capillary using Mode *A* working conditions.

served in hexane solutions kept in a refrigerator at 4 °C. Aromatic hydrocarbons are not recommended as solvents for $Ni(TFDEDTC)_2$ as the stability of $Ni(TFDEDTC)_2$ in these solvents dramatically depends on the solvent and its origin [7], which is illustrated on chromatograms shown in Fig. 3. Hexane solutions of $Ni(TFDEDTC)_2$ are stable enough, the trace impurities in hexane, however, can dramatically influence GC-ECD trace analysis of $Ni(TFDEDTC)_2$. Even purified hexane (suitable for residual analysis

of polychlorinated biphenyls PCBs) analyzed by GC-ECD in capillary columns with thicker film of a nonpolar stationary phase operated with temperature-programmed runs shows at a trace level many peaks which can overlap with a peak of $Ni(TFDEDTC)_2$ traces. Fig. 4 shows GC-ECD analyses of 1 mm^3 of hexane purified with procedure described in Experimental (B), 10 pg of $Ni(TFDEDTC)_2$ dissolved in 1 mm^3 of purified hexane (A), and chromatogram obtained by subtracting these two chromatograms (C). It can be concluded from Fig. 4 that under given conditions 10 pg of $Ni(TFDEDTC)_2$ can be detected with a relatively high reliability at signal to noise ratio $S/N = 3$. Equal detection limit was obtained analyzing purified hexane and solution of $Ni(TFDEDTC)_2$ in purified hexane by GC-ECD in another capillary column operated with different temperature working conditions (Fig. 5), even though the chromatograms obtained for hexane (background profiles) are different.

The limit of detection of Ni in water was determined by standard addition of 100 ng of $NiCl_2$ to 1 dm^3 of deionized water, which corresponds to 100 ppt of $NiCl_2$ or 45 ppt of Ni. $Ni(TFDEDTC)_2$ complex was formed by addition of 10 μg of Na(TFDEDTC) and extracted to 10 cm^3 of hexane. GC-ECD analysis of hexane extract showed 98.5 % recovery of Ni with relative standard deviation $\sigma = 4.5$ %.

CONCLUSION

It was found that the trace impurities in hexane dramatically influence GC-ECD trace analysis of $Ni(TFDEDTC)_2$ in capillary columns with thicker film of a nonpolar stationary phase operated with temperature-programmed runs. Subtraction of a hexane chromatogram from a chromatogram obtained by GC-ECD analysis of hexane solution of $Ni(TFDEDTC)_2$ enables to detect 10^{-8} mass % of $NiCl_2$ in deionized water at signal to noise ratio $S/N = 10$.

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