Fractionation of nickel species from airborne aerosols: practical improvements and industrial applications

Presently recommended methods for fractionation of airborne nickel dusts are laborious and time-consuming. A new method has been developed based on existing procedures of leaching nickel fractions from sample filters, and based on the principles of flow-injection analysis. A special sample filter holder has been constructed to be used in conjunction with the flow-injection system. In this system, soluble nickel compounds are extracted from the filter with ammonium citrate buffer, sulphidic nickel by peroxycitric acid, and metallic nickel by CuCl₂/KCl. The final dissolution of the filter by HNO₃/HCl results in the oxidic fraction. Endpoint determination of these fractions is performed by use of graphite-furnace atomic absorption spectrometry (GF-AAS). The analytical criteria of this method have been established, and the suitability of the method for application in the practice of industrial hygiene has been demonstrated.

Key words  Nickel  •  Nickel speciation  •  Nickel fractionation  •  Airborne nickel  •  Nickel sulphides  •  Nickel oxides

Introduction

It is generally recognised that the toxicity of nickel compounds depends decisively on their speciation (Pott et al. 1991). In particular, this refers to the carcinogenic potency of nickel compounds, a matter which is important for the setting of occupational standards (Aitio 1995). On the basis of an analytical fractionation of airborne nickel compounds into “water soluble”, “sulphidic”, “metallic” and “oxidic” categories, (Zatka et al. 1992) proposals have been made for the setting of differential Occupational Exposure Levels (Anonymous 1996). A simplified procedure, taking together the sulphidic, metallic and oxide nickel, has been described by Andersen et al. (1998).

The procedure of Zatka et al. (1992) involves a sequential leaching of dust samples by ammonium citrate, hydrogen peroxide/ammonium citrate, and bromine-methanol. Based on methods of the UK Health and Safety Executive (HSE), Butler et al. (1995) have described similar dissolution procedures. Materials tested included refinery dusts, welding fumes and pure nickel salts. In both methods (Zatka et al. 1992; Butler et al. 1995) the final quantitation of nickel in the fractions is performed by atomic absorption spectrometry (FAAS or ETAAS). Acceptable recoveries were obtained, for the most part in excess of 95%. However, these currently recommended nickel fractionation procedures are laborious and therefore very much time-consuming in view of a routine method.

The present paper describes a modified technique which is based mainly on the fractionation of Zatka et al. (1992), but requires a much shorter time. The separation of metallic and oxidic nickel is possible in the presence of sulphidic nickel. Specifically, a semi-automation of the sequential fractionations has been achieved by using a flow-injection system with a specially designed elution filter holder. The new procedure has been validated using dusts of different nickel species. Moreover, analytical results are presented from a pilot study of dusts from workplaces in the metal industry.

Materials and methods

Materials

For atomic absorption spectrometry a Perkin-Elmer AAS RE 5000 Z was used, equipped with a graphite furnace unit and programmer HGA-500, and with a sampler AS-40. Graphite tubes no. 091504 (Perkin-Elmer) with pyrolytic coating were used. They were found suitable for 200–300 consecutive atomisations. The reagents for the elution of different nickel species from the filters were:
(A) Water-soluble fraction: 0.1 M ammonium citrate, pH 4.4, with 0.1% (v/v) triton X-100 [Nickel carbonate: 0.1 M citric acid, brought to pH 0 with HCl, plus 0.1% (v/v) triton X-100]

(B) Sulphidic nickel: 2 parts 0.1 M ammonium citrate, pH 4.4, plus 0.1% (v/v) triton X-10; 1 part 30% (w/w) H2O2

(C) Metallic nickel: 0.25 M CuCl2, 0.3 M KCl, 0.1 M citric acid, 0.1% (v/v) triton X-100

The residue (oxidic nickel) on the filter was then dissolved separately by nitric acid/hydrochloric acid (v.i.).

Different standard aerosols of nickel, nickel(II) oxide, nickel(II) carbonate, and nickel sub sulphide were generated and collected on filters (Noldes 1999) according to the German standard VDI 2463 (Coenen 1981). For dust sample collection, cellulose nitrate filters (0.8 mm; 50 mm diameter; Sartorius, Göttin gen) were used. In experiments designed to test and calibrate the system, different amounts of nickel compounds, between 10 and 3000 µg, were applied to the filter. Elution of the nickel fractions from these filters was done as subsequently described.

Design of the filter elution system

In order to minimise the detection limit, low volumes of the filter elution fluids must be achieved. This was ensured by a special construction of the filter holder which is shown in Fig. 1. The size of the polytetrafluoroethylene (PTFE) filter holder was adjusted to filters up to a diameter of 50 mm; with a maximum diameter of the particle-loaded filter area of 40 mm. The solvent influx was distributed, via small channels (width 2 mm, depth 0.2 mm), into eight holes (0.6 mm diameter) of part B (Fig. 1), to reach the reaction chamber with the filters; it finally leaves the chamber via a hole of 1 mm internal diameter (i.d.). The total chamber volume varied, according to the filter materials used, between 0.5 and 1.0 ml. The parts A and B of the filter holder were adjusted as shown in Fig. 1. A glass fibre filter (Macherey & Nagel, Düren, MN 85/90 BF, 37 mm diameter, was centred as a cover below the bottom surface of part B, followed by the sample filter (made of cellulose nitrate, specifications v.s.). The filter holder was adapted (in- and outgoing effluents) to PTFE capillaries (0.8 mm diameter).

In order to minimise the flow resistance within the entire system, a tenside (0.1% v/v triton X-100) was added to all mobile phases (A–C, v.s., Materials section). The development of the compositions of the mobile phases for elution of nickel fractions is described in the Results section.

![Fig. 1 Construction of the filter holder to extract aerosol-loaded filters with liquid reagents (A, B, C different parts of the filter holder, see text)](image)

Using these provisions a complete solution of nickel samples can be ascertained. The entire set-up is different from that described by Zatka et al. (1992); under the final conditions described there was no practically-relevant interaction of the glass fibre cover filter material with the elution profiles.

Flow injection (FIA) system to extract nickel fractions from the filters

Using the filter holder and the solvents described above, we developed a flow-injection system, shown in Fig. 2, for elution of the different nickel (Ni) fractions. The details of the programme are shown in Table 1.

Dissolution of the nickel oxide fraction

The “open” dissolution of the Ni oxide fraction was conducted subsequently to the elution of the other fractions, according to routine procedures approved for air monitoring of Ni dusts (Coenen and Meffert 1989, Greim and Henschler 1994).

The sample filter was removed from the filter holder, transferred to a glass beaker (150 ml capacity, with loose cover glass), and 4 ml 70% (w/w) HNO3 was added. This was heated on a 150 °C plate until dissolution of the filter material occurred. Then 0.5 ml 36% (w/w) HCl was added and heating was continued until discoloration of the gas phase above the liquid took place. After the addition of 4 ml of distilled water, the whole was heated for a further 10 min and then cooled. The contents of the beaker, and rinsings (several times, n > 3) of beaker and cover, were transferred to a 25 ml calibrated bulb. It is important that no PTFE stirrer is used; nickel oxide (NiO) dust powder may attach to the porous surface of this material and thereby escape the endpoint determination by graphite-furnace atomic absorption spectrometry (GF-AAS).

Atomic absorption spectrometry

The endpoint determination was performed by use of GF-AAS in accordance with standard procedures (Coenen and Meffert 1989, Greim and Henschler 1994). The resonance wavelengths used were 352.5 nm, 341.5 nm and 361.9 nm (see also Table 4) as these are not influenced by emission lines. The temperature programmes for endpoint determination of the soluble, sulphide and oxide fractions and for the metal fraction are given in Table 2 (a and b, respectively). Normally, analyses were run in triplicate; for quantitation the standard addition method was found suitable.

Industrial application

In different areas of a metal factory using Ni and different Ni alloys, sampling of the airborne metal was performed, according to the German standard VDI 2463 (Coenen 1981). The filter instrument GS050/3 (Purucker, Berlin) was used. The sampling pump was operated at 2.5 m3/h, and the samples were taken from 1.5 m above the floor of the work area. Details have been described separately (Bolt et al. 1998).

**Results**

Elution patterns of nickel compounds from the filters

Sample filters were loaded with different Ni compounds and eluted with different solvents by the filter holder system shown in Fig. 1. Flow rates were kept at approximately 1 ml/min (minimally 0.5 ml/min, maximally 1.6 ml/min).