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XANES and Zatka speciation methods were compared for application in epidemiology of occupational aerosols from sulphidic nickel production.

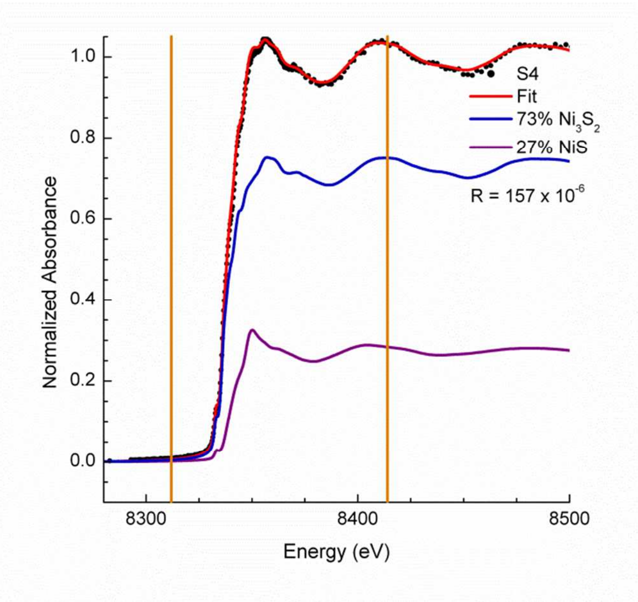

Figure 1. Nickel K-edge XANES spectrum of a Sulphidic sample fit with component spectra Ni_3S_2 and NiS.

Sulphidic nickel production has been associated with occupational respiratory cancer. After more than a century of production, there remains a pressing need to develop complete speciation knowledge for the industry. Europe's proposed occupation exposure limits (OEL) for nickel compounds reflect older speciation understanding. Regulatory initiatives such as that in Europe, coupled with the need for proper protection within the refinery setting justifies the importance of developing new, accurate speciation methodology. The application of X-ray absorption near-edge structure (XANES) spectroscopy enables the direct identification of unique nickel compounds within an aerosol matrix, and offers a chemical basis to advise regulatory initiatives to protect worker and public health in the development of OEL's and ambient air quality limits.

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Comparison of nickel speciation in workplace aerosol samples using sequential extraction analysis and X-ray absorption near-edge structure spectroscopy

Lisa L. Van Loon,*[a] Cassidy Throssell,[b] and Michael D. Dutton[c]

There is a pressing need to further develop speciation knowledge of Ni workplace aerosols as the Zatka sequential extraction method used until now to speciate workplace Ni exposures has limitations. Here we compare the Zatka and XANES methods and evaluate XANES spectroscopy as a more appropriate and accurate technique for identifying nickel species in workplace aerosols. XANES spectroscopy is capable of identifying unique Ni species in the unaltered samples. Our findings indicate some significant departures in speciation assignment between the Zatka and XANES methods. In particular, the Zatka method can overestimate the soluble Ni fraction and it may underestimate the sulphidic and metallic fractions in some samples. Of particular importance, XANES is able to identify component sulphidic species. This information can lead to more accurate exposure matrices and more refined epidemiological analysis of respiratory cancer causation in sulphidic Ni processing.

Introduction

It has been known for more than 75 years that certain job categories in the production of Ni from sulphidic ores had elevated risk of respiratory cancer[1]. The current understanding of the carcinogenic potential of the most prominent Ni species in sulphidic Ni production (nickel subsulphide (Ni_3S_2), nickel oxide (NiO), nickel metal (Ni^0), and soluble nickel (primarily nickel sulphate, $NiSO_4$) has been determined from a combination of animal testing (of pure compounds) and human epidemiological study[2]. There can be no doubt that elevated rates of respiratory tract cancer are associated with sulphidic Ni processing at several facilities worldwide, but all epidemiological evidence regarding the inhalation carcinogenicity of Ni has relied on historical exposure matrix reconstruction to allocate risk to individual Ni species. Exposure estimates have been limited by a lack of quantitative exposure information from periods prior to the 1970s[1, 3-7], such that these estimates included reliance on non-quantitative measures such as subjective recollections by personnel upon retrospective interview.

Certainly, the meaningful epidemiological analysis of respiratory cancer causation in sulphidic Ni processing cannot be considered complete in the absence of accurate identification of the identity and amounts of the different Ni species to which workers were exposed.

Analysis of Ni in the workplace first relied upon time-consuming colorimetric approaches such as the dimethylglyoxime method[8] prior to the availability of atomic absorption spectrophotometry in the late 1950s. In Ontario, air sampling by konimeter was required only as of 1959, and Inco's Occupational Exposure Monitoring Program (OEMP) began in 1977. Ni fractionation in workplace air was out of the question before the publication of the Zatka sequential extraction method in 1992.[9] This wet chemistry method was developed to quantify four types of airborne nickel found in the workplaces of an integrated sulphidic-nickel smelter/refinery. The sequential extraction method differentiates groups of nickel compounds based upon chemical behaviour. The nickel is classified as soluble, sulphidic, metallic, or oxidic via four leaching steps. The method is sensitive to the sample composition. This method has been the predominant speciation methodology for the Ni industry for the past 20 years.

The Zatka method suffers from limitations seen with all sequential leaching speciation methods[10-13], including: (1) incompatibility of particle size and filter pore size, with small particles passing the filter regardless of the Ni species present; (2) kinetic limitations of extractions, in that each extraction step occurs over limited time periods, possibly leading to incomplete extraction; (3) formation and redistribution of new chemical phases; and (4) non-homogeneity of particles and presence of coatings limiting access of extractant to the relevant chemical species. In spite of these shortcomings, the Zatka method provided a quantitative estimate of speciation within the industry and was used in epidemiological studies of respiratory cancer risk in the nickel industry[7].

To overcome the shortcomings of the Zatka method, an alternate method for speciating nickel in occupational aerosols has been developed using synchrotron X-ray absorption near-edge structure (XANES) spectroscopy. XANES is capable of probing the local structure of specific elements *in-situ* without requiring physical separation of the aerosols from the filter papers. Both crystalline and non-crystalline nickel compounds can be identified on the filters, providing information on oxidation state, the coordination environment, complexation/bonding, and molecular geometry[14]. Unique compounds can be identified by measuring the Ni 1s (K-edge) XANES spectrum of each sample in conjunction with a series of standard Ni compounds. Linear combination fitting (LCF) analysis compares the sample spectrum with spectra derived from weighted mixtures of the standards, with the selection of initial standards being guided by metallurgical process knowledge. Synchrotron radiation techniques have been applied to the characterization of Ni in a variety of environmental samples in recent years, including combustion emissions[15], coal and its ash by-products[16], residual oil combustion ash[17-19], combustion products[20], and soils near a Ni refinery[21]. To our knowledge, this is the first study using XANES spectroscopy to identify Ni species in occupational aerosol samples.

It is unfortunate that, after a century of operation, it can still not be said that the speciation of occupational aerosols in the primary sulphidic Ni production industry is definitively understood. There remains a pressing need to further develop speciation knowledge for the industry. Here, we compare the Zatka sequential extraction method and XANES spectroscopy, and evaluate XANES spectroscopy as a more appropriate and accurate technique for identifying nickel species in workplace aerosols.

Experimental

Occupational aerosol sample collection

Fifty-four sets of stationary inhalable-fraction occupational aerosol samples were collected in triplicate (n=47) or duplicate (n=7) at twelve locations within Vale Canada's Nickel Smelter and Refinery in Copper Cliff, Ontario (CCNR) and at four locations within Vale's Port Colborne Refinery (PCR) in Port Colborne, Ontario. The sampling was performed using 25 mm IOM 7-hole cassettes with pre-weighed Versapore membrane filters (pore size of 1.2 μm) at a flow rate of 2 $L \cdot min^{-1}$, for 24 hours. The filter cassettes were purged with nitrogen following post-sampling flow rate checks. The 2-3 samples for each set were collected simultaneously. One filter was used for the Zatka sequential leaching analysis and one for the XANES spectroscopic analysis and the third sample is not reported here.

Zatka Sequential leaching analysis

Zatka analyses were conducted at Vale's central lab in Copper Cliff, ON, Canada using the method as found in the literature[9], with the following differences: Peroxide leach solution was made and adjusted to pH 4.0-4.2 with ammonia or citric acid. Soluble Ni was determined by leaching the air filters with 35 ml of ammonium citrate solution for 1 hour. Sulphidic Ni was leached for 60 minutes twice with 35 ml of peroxide-citrate solution. Oxidic Ni was digested in 10 ml of concentrated HNO_3 and 5 ml of $HClO_4$, with additional aliquots of acid being added until the solution was clear. Ashed and digested solutions were stabilized with 0.4 ml of scandium solution and diluted to 10 ml with water for analysis by ICP. The mass of nickel extracted in each step was quantified and the relative percent contribution was calculated. The results for individual samples are found in the Electronic Supplementary Information (ESI).

X-ray Absorption Near-Edge Structure (XANES) Spectroscopy

Nickel K-edge XANES spectra were recorded on the Hard X-ray Micro Analysis (HXMA) beamline (06ID-1) at the CLS, a 2.9 GeV synchrotron facility located at the University of Saskatchewan, during the period November 2007 to March 2009. The HXMA beamline uses a superconducting wiggler operating at 1.9 T as a source point for tuneable X-rays. The incident beam was monochromatized using a double crystal monochromator equipped with Si (220) crystals. The beam size for all samples was 1.0 x 4.0 mm. The incident X-rays were detuned between 50% - 70% to minimize the higher harmonics produced by the monochromator at the Ni K-edge. Spectra for the sample and standard compounds were collected to $k=9$ $Å^{-1}$. Calibration of the energy position was done by collecting a Ni foil (6μm, EXAFS Materials, Inc.) spectrum in transmission mode. Strips cut from the sample filters were mounted on a sample holder using Kapton tape. Sample spectra were collected in fluorescence mode using the Lytle Box detector or 32-element Ge solid state detector, depending on the sample concentration. The spectra of standard nickel compounds were collected in transmission mode. A minimum of two scans were recorded for each sample. Nickel concentrations on blank filters were below the detection limits.

The sample spectra were analysed using the X-ray absorption spectroscopy data processing software Athena, version 0.8.56[22]. Sample spectra were calibrated at the Ni K-edge to 8333 eV using the 2nd derivative spectrum of the Ni foil. Spectra were background-corrected by subtracting a straight line fit to the pre-edge from the entire spectrum. The spectra were normalized to a per-atom basis by using a straight line fit to the post-edge region of the XANES spectrum. Least squares linear combination fitting (LCF) was used to identify the predominant nickel species present in each sample by fitting each sample spectrum with weighted mixtures of the standard Ni compounds.

In this context, it is essential that the LCF analysis of XANES spectra to speciate occupational aerosols from the sulphidic Ni production industry be thoroughly assessed. To evaluate the ability of XANES to accurately identify representative Sulphidic, Oxidic, Metallic, and Soluble Ni species in mixtures, two four-component Ni mixtures were prepared containing $NiCO_3$ or $NiSO_4 \cdot 6H_2O$, Ni^0, NiO, and NiS. It should be noted that the mixtures did not include both $NiCO_3$ and $NiSO_4 \cdot 6H_2O$

because their XANES spectra are very similar and cannot be distinguished using the linear combination fitting method. Although in the fitting procedure, E_0 values were not allowed to vary and the fits were not constrained to sum to 100%, both mixtures did indeed sum to 100%. Each fit was carefully tested for robustness against the complete Ni spectral library. The fits were conclusive, suggesting accuracy within ±5%. The LC fitting of the XANES spectra for these two mixtures containing the key expected species for the workplaces under study suggests that the use of XANES for speciation of Ni in the sulphidic Ni processing industry has considerable potential (The spectra and % composition results are found in the Electronic Supplementary Information.).

X-ray Photoemission Spectroscopy (XPS)

Photoemission spectra were recorded at the High Resolution Spherical Grating Monochromator (SGM) 11ID-1 beamline at the CLS. For all measurements, the incident photon beam was the 1st harmonic collected from the SGM 45 mm planar undulator. The silicon strip was selected on the pre-monochromator optics. Either the 1100 lines/mm (medium energy) grating or the 1700 lines/mm (high energy) grating was selected to maximize the photon flux (~2×10^{12}/s/100mA). Two photon energies were used: 1000 eV and 2000 eV. The slit width was set at 100 μm and the minimum resolutions were 150 meV at 1000 eV and 250 meV at 2000 eV. Spectra were collected with a Scienta SES100 photoelectron energy analyzer with a pass energy of 200 eV for the 2000 eV photon energy experiment and 50 eV for the 1000 eV photon energy experiment. The nickel nanopowder samples were mounted on carbon tape. The adventitious carbon 1s and nickel 2p regions were scanned alternately. The energy scale was calibrated using the adventitious carbon 1s spectrum (binding energy (BE) = 285 eV)[23]

Materials

The standard nickel compounds used in this study were NiS and Ni_3S_2 (Pure samples of NiS and Ni_3S_2 were synthesized by Vale Canada Limited), $NiSO_4 \cdot 6H_2O$ (Alfa Aesar, 99.97% min metals basis), $NiCO_3$ (Alfa Aesar, 99% Anhydrous), $NiCl_2 \cdot 6H_2O$ (Alfa Aesar, 99.95% metals basis) Ni^0 (Inco 123 powder, Vale Canada Limited), Ni^0 (Sigma-Aldrich, <100 nm particle size nanopowder, 99.9% trace metal basis, used for the XPS study), NiO (Sigma-Aldrich, 99.999%), $Ni(OH)_2$ (Alfa Aesar, Ni 61%) and $NiFe_2O_4$ (Sigma-Aldrich, 98+% <50 nm particle size nanopowder).

The standards were characterized for purity to determine their suitability for Ni species quantification. It was found that commercially available sulphidic nickel compounds can contain mixtures of sulphidic Ni species. For this work, NiS and Ni_3S_2 were synthesized and characterized independently by Vale Canada Limited. The standards were all analysed by XRD (Rigaku Rotaflex RU-200, X-ray Diffraction Laboratory, Department of Geological Sciences, University of Saskatchewan). The XANES spectra of all the standard Ni compounds are shown in Figure 1.

Results

For the purposes of this study, the sampled work areas have been divided into five operationally-defined groups based on the metallurgical processes, materials being handled, and spatial orientation of the processing activities at the different sampling locations. The sampling locations were selected based on the expected process chemistry. Samples collected from matte processing and handling are expected to contain predominantly sulphidic nickel species. In this study, this sample group is named *Sulphidic*. Samples collected from locations where processing activities such as roasting occur are expected to contain predominantly oxidic nickel species. This sample group is named *Oxidic*. Samples collected in areas where common processing activities produce mixed aerosols of oxidic and sulphidic nickel species are named *Sulphidic/Oxidic*. Samples collected in work areas where activities include post-processing functions such as shearing, powder packaging, and shipping of metallic nickel product are named *Metallic*. Finally, samples collected from the feed unloading and cobalt precipitation areas of the Port Colborne Refinery are expected to contain primarily nickel carbonate. This sample group is named *Carbonate*. The sampling locations are listed in Table 1. The overall results for each sample group analyses are presented in Table 2. Results for individual samples are presented in the electronic supplementary information (ESI).

Zatka sequential extraction

The Zatka method takes advantage of the differential solubility of individual Ni compounds under specific chemical conditions. Ni is leached from the aerosol sample sequentially into four different fractions: soluble, sulphidic, metallic, and oxidic [24].

Thirteen samples were grouped as *Sulphidic*. The Zatka extraction determined that sulphidic nickel was the predominant fraction present on the filters ((71 ± 13)%). The soluble nickel fraction accounted for 13% (± 4%) of the Ni present, while the metallic and oxidic Ni fractions accounted for 4% (± 3%) and 11% (± 13%) of the total Ni, respectively.

Eight samples from two locations were grouped as *Oxidic*. The Zatka extraction identified 66% (± 21%) of the Ni present as oxidic nickel, with the sulphidic Ni fraction accounting for 20% (± 13%) of the Ni. Soluble and metallic Ni fractions accounted for the remaining 14%. The percentages of Ni in the oxidic and sulphidic Ni fractions for the two sampling locations were quite different. The FEN Bulk Loading samples contained ~ 90% oxidic Ni and ~ 5% sulphidic Ni and the Clydach Landing samples contained ~ 50% oxidic Ni and ~ 25% sulphidic Ni fractions.

Nine samples were grouped as *Sulphidic/Oxidic* based on the processing occurring at the sampling locations. The Zatka sequential extraction identified 66% (± 14%) as oxidic Ni and

22% (± 3%) as sulphidic Ni. The remaining 12% was identified as belonging to either the soluble or metallic Ni fractions.

Six samples were grouped as *Carbonate*. The Zatka analysis found the Ni distributed as 32% (± 9%) soluble Ni fraction, 32% (± 9%) sulphidic Ni fraction, 13% (± 4%) metallic Ni fraction, and 23% (± 6%) oxidic Ni fraction.

For the eighteen samples that were grouped as *Metallic* based on processing occurring at the sampling locations, the Zatka analysis identified oxidic Ni as the predominant fraction. The 12 Copper Cliff Nickel Refinery (CCNR) samples were identified as 76% (± 7%) oxidic Ni fraction and 15% (± 5%) metallic Ni fraction. The remaining 9% was divided between the soluble and sulphidic Ni fractions. The 6 Port Colborne Refinery (PCR) samples were identified as 28% (± 7%) oxidic Ni fraction, 21% (± 5%) metallic Ni fraction, 17% (± 8%) sulphidic Ni fraction, and 34% (± 8%) soluble Ni fraction, Table 2.

XANES spectroscopic analysis

XANES spectroscopy is an element-specific method capable of determining the local environment for the atom of interest. Analysis of the collected aerosol samples occurs directly without any physical or chemical manipulation required for sample preparation. The sample can be examined dry or wet. The nickel species here were measured directly on the sample filters. Identification of the unique nickel species present in the sample occurs by comparing the sample spectrum against well-characterized reference spectra, shown in Figure 1. Distinctive spectral features enable the differentiation of component nickel species. For example, the sulphides tend to have fairly flat spectra, while the oxides and salts have a sharp first peak at ~ 8340 eV.

The XANES analysis identified unique Ni species but in Table 2 the results have been grouped using the Zatka fractions (soluble, sulphidic, metallic, and oxidic) to facilitate comparison between methods. The XANES results provide additional chemical speciation important information, including the relative concentrations of NiS and Ni_3S_2 in each sample.

In nine of the thirteen samples grouped as *Sulphidic*, only nickel subsulphide (Ni_3S_2) and nickel sulphide (NiS) were identified by XANES (Table 2). The samples were either found to be 100% Ni_3S_2, or were a mixture of NiS and Ni_3S_2. A representative *Sulphidic* group (S4) XANES spectrum along with the LC fit and component spectra are shown in Figure 2. XANES spectra of all the individual samples can be found in the ESI. Four of the samples in the *Sulphidic* group were found to contain Ni_3S_2 (67 ± 10%), oxidic Ni (14 ± 11%), and metallic Ni (19 ± 11%).

The eight samples grouped as *Oxidic* were found to contain 69% (± 17%) NiO. The sulphidic component was split with 22% (± 23%) Ni_3S_2 and 9% (± 13%) NiS. There was significant variation in the Ni species present in the different samples; the large standard deviations reported reflect that many samples contained either Ni_3S_2 or NiS. A representative *Oxidic* group (O1) XANES spectrum along with the LC fit and component spectra are shown in Figure 3.

The nine samples grouped as *Sulphidic/Oxidic* were found to contain 55% (± 23%) NiO, 28% (± 27%) Ni_3S_2, and 17% (± 29%) NiS. Similar to the *Oxidic* samples, these samples were found to contain either Ni_3S_2 or NiS in addition to NiO, accounting for the large standard deviations. A representative *Sulphidic/Oxidic* group (OS1) XANES spectrum with the LC fit and component spectra are shown in Figure 4.

Twelve samples collected at CCNR and 6 samples collected at PCR were grouped as *Metallic*. Eleven of the 12 CCNR samples were determined by XANES analysis to contain 96% (± 4%) Ni^0 and 4% (± 4%) Ni^{2+} (fit as $NiSO_4{\cdot}6H_2O$). The twelfth sample (sample ID M12) contained 70% NiO and 30% NiS. It appears to be an outlying sample and was not included in the location average. Relative per cent contributions in three of the six PCR *Metallic* samples could not be determined quantitatively, because their total loading was much lower than the other samples, and are therefore not included in the location average. The sampling location is a relatively clean area, with the only activity being nickel shearing. The likely species present were an ionic Ni^{2+}, represented here with $NiCO_3$ or $NiSO_4{\cdot}6H_2O$, NiO, and Ni^0. (LCF relies on unique features in the spectra and $NiCO_3$ and $NiSO_4{\cdot}6H_2O$ have very similar spectra, reflecting the molecular environment of the Ni^{2+} ion. In a complex mixture containing ionic Ni^{2+} salts it can be difficult to identify Ni beyond determining that it is ionic Ni^{2+}.) The remaining 3 samples were found to contain ~85% (± 7%) Ni^0 and ~15% (± 7%) Ni^{2+} ($NiSO_4{\cdot}6H_2O$ or $NiCO_3$). A representative *Metallic* group (M1) XANES spectrum with the LC fit and reference compounds are shown in Figure 5.

For the six samples grouped as *Carbonate*, the XANES analysis identified $NiCO_3$ in each sample, but the amount varied widely (29% to 80%). The samples contained a variety of other nickel compounds, including NiS (2 samples), NiO (1 sample), Ni^0 (1 sample), and $NiSO_4$ (3 samples). A representative *Carbonate* group (C1) XANES spectrum with the LC fit and reference compounds are shown in Figure 6.

Discussion

A comparison of the speciation assignments by the Zatka method and XANES spectroscopy of these 54 aerosol samples reveals five major observations:

1. The Zatka method always detects all four fractions (soluble, sulphidic, metallic, and oxidic), with soluble Ni being the second largest fraction in three of the sample types (*Sulphidic*, *Sulphidic/Oxidic*, and *Carbonate*) and the largest fraction in the *Metallic* samples from PCR. Even among the Oxidic samples, 10% is attributed to the Soluble Ni fraction by the Zatka method. In these same sample groups, XANES detected $NiSO_4{\cdot}6H_2O$ only in the CCNR *Metallic* samples (4%) and in the PCR Carbonate samples (19%), but did not identify soluble Ni in the *Sulphidic*, *Oxidic* or

Sulphidic/Oxidic samples. Also, XANES did not identify Ni^0 in the *Oxidic* and *Sulphidic/Oxidic* sample groups.

2. For the *Metallic* samples, XANES identified Ni^0 as the primary species, whereas Zatka did not.
3. For the *Sulphidic* samples, both XANES and Zatka identified the sulphidic Ni fraction as the primary component, although Zatka identified all four fractions as being present, with soluble Ni as the second largest fraction. XANES did not identify soluble or metallic Ni in these samples. XANES was able to identify two constituent species of the sulphidic fraction, Ni_3S_2 and NiS. During the refining process, pentlandite is converted to nickel subsulphide. The material is slow-cooled to make large granules of $Ni_3S_2 + Ni^0$ in the matte. The smelter is a mixed workplace and the identification of either Ni_3S_2 or $NiS + Ni_3S_2$ likely reflects the sampling locations of mixed air in the smelter. The Zatka method is unable to discriminate between sulphidic components.
4. For the *Sulphidic/Oxidic* samples, XANES and Zatka both identified mixed sulphidic/oxidic fractions as the dominant species, but no soluble or metallic Ni species were identified by XANES.
5. For the *Oxidic* samples, both methods identified Ni-oxides as the primary species, accounting for nearly 70% of the Ni.

These findings indicate some significant departures in speciation assignment between the modified Zatka method used by Vale Canada Central Labs in Copper Cliff, ON, a variant of the most prevalent Ni fractionation method currently used, and XANES, a method not previously applied to the speciation of occupational Ni aerosols. Given that the Zatka method has strongly influenced the current understanding of historical exposures in the recent epidemiological literature, it is important to ensure that the Zatka fractionation assignments are appropriate. Furthermore, the potential replacement of Zatka with a new method requires that the replacement method be validated.

The Zatka method identified approximately 10% soluble Ni in the *Sulphidic*, *Oxidic*, and *Sulphidic/Oxidic* sample groups. This is a large enough amount that, assuming homogenous distribution over the sample filters, soluble Ni should have been detected by XANES. That it was not suggests that in fact, the soluble fraction identified by the Zatka analysis was not truly soluble Ni. Three possible explanations follow.

Conard[12] proposed that reactions between nickel sulphides and non-Ni metal interferences to form soluble nickel species could lead to incorrect reporting of sulphidic Ni as soluble fraction in certain sample types in the Zatka method. Additionally, other metal compounds that are soluble in the ammonium citrate leaching solution (pH ~ 4.4) can also be leached and included in the measured mass.

It is possible that smallest particles could be leached by virtue of their high surface area to volume ratio. The solubilisation of Ni from particles containing Ni species that would otherwise be expected to leach in later steps may be enhanced under the assay conditions of the initial leaching step.

These three factors could all contribute to the enhanced quantity of apparent soluble Ni in these occupational aerosol samples.

It is also possible that very fine particles may pass through the filters after the initial (soluble) leaching step in the Zatka analysis. This could be due, in part, to a reduction in size during this leaching step, facilitating the loss of these particles to the soluble filtrate. Filtration in the Zatka method uses 0.45 μm filters, so the losses to filtrate at any step would be a function of particle size distribution and chemical composition. Since the air filters used for collection of the aerosols have a nominal pore size of 1.2 μm, it may seem counter-intuitive that particles smaller than 0.45 μm would be present in the sample during the Zatka analysis. However, samples are collected at low flow rates in a medium (air) with extremely low viscosity and for periods up to 24 hours. Particle size distributions of occupational air samples can easily contain particles smaller than 0.45 μm even though nominal pore size is 1.2 μm. The speciation study of Andersen[24], which has heavily influenced thinking on soluble Ni exposures, used Blauband filters having a 2 μm pore size in a modification of the Zatka method. This could have enhanced apparent contributions to the soluble fraction.

For the *Metallic* samples, the Zatka method and XANES identified different primary components, with XANES identifying Ni^0 as the primary component while the Zatka method identified oxidic Ni as the primary fraction. It is known that Ni powders have thin oxide surfaces that occur as the powders are passivated during formation. It has been postulated[12] that these oxide surfaces prevent the bromine-methanol extractant from dissolving the underlying metallic Ni phase in the metallic extraction phase of the Zatka method. The resulting undissolved metallic Ni would then be reported as oxidic Ni by default. Since this nickel oxide shell would be only nm thick, it represents only a small percentage of the total Ni and it is therefore reasonable that NiO did not contribute to the Ni K-edge XANES spectra. XPS of nickel metal powders also identified the presence of NiO coatings on the surface of Ni metal particles[25]. Comparison studies of predominantly oxidic nickel particulate matter found that the Zatka method over-reported the amount of metallic nickel and under-reported the amount of oxidic nickel where the XANES analysis identified no Ni^0 [26, 27].

To determine if the metallic nickel present in the samples is likely coated with an oxidic layer, preventing its extraction in the sequential leaching analysis, synchrotron-based X-ray photoemission spectroscopy (XPS) was used to examine the surface of Ni nanopowder (Figure 7). Spectra of the Ni 2p region were collected using photon energies of 1000 and 2000 eV. It is clear that the Ni species present at the surface (PE = 1000 eV, penetration depth ~ 0.7 nm[28]), Figure 7 upper half, and deeper in the nanopowder (PE = 2000 eV, penetration depth ~ 1.6 nm[28]), Figure 7 bottom half, are different. The surface spectrum has a peak at 856.4 eV, indicating the presence of Ni_2O_3[23, 28]. The spectrum collected at PE = 2000 eV indicates the presence of Ni metal by the peak present at 852.5

eV. There is a smaller peak present at 855.5 eV which indicate the presence of some NiO.[23] The surface of the Ni^0 nanopowder is clearly coated with a thin oxidic layer. Presumably, the presence of this film could prevent leaching of Ni metal by methanol/bromine in the third Zatka leaching step. In such a case, both the oxidic Ni and the oxide-coated Ni^0 would report to the final, oxidic step of the Zatka method. The Zatka analysis would then incorrectly report both a lower Ni metal fraction percentage and a greater percentage of oxidic Ni, as has been noted previously[12].

With sequential leach methods, there are necessary trade-offs to accurately separate certain chemical phases. The standard Zatka method, still in use by Vale Canada Limited, uses a very short metallic leach as per the original paper[9]. This is to minimize dissolution of basic nickel salts and nickel hydroxides. As a result, samples containing high proportions of metallic Ni may be under-estimated. A longer extraction time is necessary for predominantly metallic samples. Luk *et al* also found that the Zatka method under-reported metallic nickel and found that longer extractions were required[29]. Later findings using Inco 123 powder identified a need for three 5-minute leaches with Br-methanol solution to accurately recover metallic nickel samples (Vale Canada Limited, unpublished data). Luk *et al*[29] also found that the Zatka method under-reported metallic nickel in samples containing a large proportion of Ni^0 and, determined that longer leaching (>20 min) with Br-methanol solution was appropriate for such samples. This highlights that sequential extractions require advanced knowledge of the samples in order to accurately fractionate them.

The differences between the Zatka and XANES results for the *Carbonate* samples may be related to several phenomena. First, XANES was unable to clearly speciate three of the six *Carbonate* samples, which had the lowest Ni levels among the 54 samples (approximately 0.0054 mg/m^3). The inability of XANES to quantitatively speciate these particular samples may have been related to the low signal. Second, use of ammonium citrate in the first (soluble) extraction stage is likely to have a major impact on speciation assignments when Ni carbonate is present. Ammonium citrate solubilizes even sparingly soluble oxidic nickel carbonates in addition to the labile salts of Ni in the first, soluble fraction in the Zatka method[30]. This citrate effect would result in the Zatka method over-reporting soluble Ni by unknowingly including some $NiCO_3$ in the soluble fraction instead of in the oxidic fraction, where it would be expected[9].

The Ni carbonate-soluble Ni anomaly has been recognized for some years. The ICNCM report[1] noted that there were differences in how individual companies reported the speciation of samples expected to contain nickel carbonate, with some companies reporting nickel carbonate and hydroxide as soluble, whereas others reported carbonates as insoluble.

The Zatka method is an operationally-defined analytical method and likely suffers from many of the issues associated with sequential leaching speciation methods[13]. XANES is unable to distinguish between Ni-sulphate and Ni-carbonate salts due to similarities in the Ni molecular environment. (Ni^{2+} halides such as $NiCl_2$ can be distinguished because of the different chemical environment experienced by the Ni^{2+} ion.) In spite of this, these two lines of evidence begin to allow a more complete understanding of the complicated nature of Ni speciation and the barriers it presents to the true identification of certain Ni species in occupational aerosols. Our data support the view that caution should be used in interpreting Zatka results for samples containing Ni carbonate.

In a LCF analysis of XANES spectra, the library of reference spectra is critical to good speciation assignments and must be selected for specific samples. The expected sample chemistry is an important consideration in the analysis. Failure to consider the processing chemistry can lead to an incomplete speciation analysis. In this case, the nickel refining process informed the reference material selection. The development of pure synthesized references was key to the sulphidic speciation since commercially available materials may not be pure. For example, commercially available nickel sulphide is predominantly heazelwoodite, not NiS or other nickel sulphides. (For example Tirez *et al*[27] includes a commercially available nickel sulphide in the analysis. The spectrum is that of nickel subsulphide, when compared with the spectra shown in Figure 1.)

An advantage of the XANES analysis compared with the Zatka sequential extraction is the ability to identify unique Ni species in the sample. Importantly, the spectra of nickel sulphide and nickel subsulphide (Figure 1) have unique features, enabling their differentiation. The primary mineral form of Ni mined and processed at Vale's Sudbury operations is pentlandite ($Ni_{4.5}Fe_{4.5}S8$) in which Ni, Fe, and trace amounts of Co exist in solid solution. No pure pentlandite standards were available for this study so synthetic NiS (millerite) was used to approximate pentlandite and is expected to have a similar environment for the Ni ions. Small differences between the sample spectra and the LCF fit are likely due to element substitutions in the sample material when compared with the pure reference compounds selected for the LCF analysis.

Previous evaluations of sequential leaching speciation procedures have shown that these methods can sometimes lead to incorrect speciation assignments[13], particularly for Ni[12, 26]. Soluble Ni has been routinely identified in previous speciation studies of workplace aerosols using the Zatka method[24, 31-33]. In this study, the Zatka method also identified soluble Ni in all samples but XANES did not. That XANES did not identify the presence of soluble Ni in the samples suggests that all the previous Ni speciation data from the Ni industry (based on the Zatka sequential extraction protocol) should be re-evaluated using techniques like XANES. The previous work of Vincent[32] included samples from the Vale Copper Cliff smelter (denoted as Company A smelter and refinery) that were from similar locations as the current samples and were speciated using the Zatka method. The speciation results of Vincent very closely mirror those of the current study when analysed by the Zatka method and are expected to have overestimated the fraction of soluble Ni present. A similar situation may have occurred with samples studied by others,[24, 31] as the sequential extraction analyses were performed at Inco's J. Roy Gordon Laboratory using the standard Zatka method.

An extensive regulatory risk assessment of several nickel compounds has recently been undertaken in Europe. The risk assessment relied upon the speciation information available at the time to conclude that soluble nickel is commonly present in sulphidic Ni production operations. However, the data presented here do not indicate that soluble nickel is present in Vale's sulphidic nickel processing facilities in Copper Cliff, ON.

Conclusions

Fifty-four occupational air samples from an integrated Ni smelter and carbonyl refinery were examined in parallel using a variation of the Zatka leaching method and XANES spectroscopy. The LCF analysis of the XANES spectra are in disagreement with sequential leach results with respect to the presence of soluble nickel. In particular, in the same smelting workplaces where the Zatka method has previously identified soluble Ni[32], this study also found 10% soluble Ni using the Zatka method. However, no soluble Ni was detected by LCF analysis of the collected XANES spectra. Our findings suggest that the common view of Ni speciation in sulphidic-Ni production environments may be incomplete. Although the samples reflect present operational conditions, the head to head comparison of XANES and sequential leaching allows us to reflect upon the chemical nature of historical exposures. More study is needed, but this preliminary study of a relatively large number of samples suggests that tools are available to further refine retrospective exposure assessment.

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Notes and references

[a] Canadian Light Source Inc., Saskatoon, SK, Canada.
[b] Vale Canada Limited, Copper Cliff, ON, Canada.
[c] Vale Canada Limited, Mississauga, ON, Canada.

Electronic Supplementary Information (ESI) available: [A summary of all experimental results can be found in Tabular Summary of Experimental Data.xlsx]. See DOI: 10.1039/b000000x/

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Table 1. Sampling locations within the Copper Cliff nickel smelter and refinery and Port Colborne refinery classified as a function of expected metallurgy based on the process chemistry.

Operationally-Defined Classification	**Sample ID**	**Location**
Sulphidic	S1 - S3	Copper Cliff Smelter:Separation:Jumbo Cells
	S4 - S6	Copper Cliff Smelter:Separation:Ground Floor Ball Mills 2a&2b
	S7 - S9	Copper Cliff Smelter: Casting: #89 Control Panel
	S10 - S13	Copper Cliff Nickel Refinery: Nickel Refinery Converter: Track Hopper
Oxidic	O1 - O3	Copper Cliff Smelter:Shipping:FEN Bulk Loading
	O4 – O8	Copper Cliff Nickel Refinery:Nickel Refinery Converter Building:Clydach Landing
Oxidic/Sulphidic	OS1 – OS4	Copper Cliff Nickel Refinery: Nickel Refinery Converter:Behind Converters – ‘944
	OS5 – OS6	Copper Cliff Nickel Refinery: Nickel Refinery Converter:#17 Charging Conveyors
	OS7 – OS9	Copper Cliff Smelter: Fluid Bed Roaster: #2 Gatefeeder
Metallic	M1 – M4	Copper Cliff Nickel Refinery:Inco Pressure Carbonyl:#1 Local Powder Packaging
	M5 – M9	Copper Cliff Nickel Refinery: Inco Pressure Carbonyl:Battery Powder Packaging
	M10 – M11	Copper Cliff Nickel Refinery: Inco Pressure Carbonyl:Packaging and Shipping - OSP
	M13 – M15	Port Colborne: Rounds: Automatic Shearing

	M16 – M18	Port Colborne: Rounds: Ten Kilo Bag Line
Carbonate	C1-C3	Port Colborne: Cobalt Precipitation Area
	C4-C6	Port Colborne: Copper Refinery Electrowinning Division Truck Unloading

Table 2. Percent compositions of the Ni fractions determined by the Zatka sequential extraction and XANES LCF analyses.[a]

Operationally-Defined Classification	**Sample ID**	**Zatka**				**XANES**						
		Soluble (%)	Sulphidic (%)	Metallic (%)	Oxidic (%)	Soluble (%)	Sulphidic (%)			Metallic (%)	Oxidic (%)	Carbonate (%)
							Total	Ni_3S_2	NiS			
Sulphidic	S1 – S6	15.6 ± 2.8	75.2 ± 2.7	3.3 ± 2.5	5.9 ± 3.2	0	100	86.2 ± 15.4	13.8 ± 15.4	0	0	
	S7 – S9	10.6 ± 2.3	79.7 ± 9.8	2.1 ± 0.8	7.6 ± 6.9	0	100	81.7 ± 31.8	18.3 ± 31.8	0	0	
	S10 – S13	12.0 ± 4.9	59.5 ± 18.2	7.4 ± 1.9	21.1 ± 20.6	0	67.3 ± 10.0	67.3 ± 10.0	0	19.0 ± 11.2	13.8 ± 11.4	
Oxidic	O1 – O3	1.7 ± 0.4	5.8 ± 2.2	1.1 ± 0.7	91.4 ± 2.4	0	18.6 ± 4.6	5.3 ± 9.2	13.3 ± 12.2	0	81.3 ± 4.6	
	O4 - O8	14.4 ± 5.7	28.4 ± 5.9	6.2 ± 0.7	51.0 ±	0	38.6 ±	32.2 ±	6.40 ±	3.2 ± 7.2	58.2 ±	

					5.5		14.6	22.9	14.3		14.6	
Oxidic/Sulphidic	OS1 – OS6	9.2 ± 3.7	11.6 ± 3.0	4.5 ± 2.3	74.7 ± 5.0	0	30.1 ± 7.1	19.2 ± 16.2	11.0 ± 17.1	0	69.8 ± 7.1	
	OS7 – OS9	6.4 ± 0.8	43.6 ± 5.5	2.1 ± 1.2	47.9 ± 6.1	0	74.3 ± 11.0	46.0 ± 40.3	28.3 ± 49.1	0	(25.7 ± 11.0	
Metallic	M1 – M11[b]	4.0 ± 2.4	5.3 ± 3.2	14.4 ± 4.9	76.3 ± 6.4	0	0	0	0	96.5 ± 3.6	0	
	M16 – M18[c]	33.9 ± 8.0	16.7 ± 8.4	1.4 ± 5.1	28.0 ± 7.0	0	0	0	0	74.3 ± 19.1	0	25.7 ± 19.1
Carbonate	C1 – C6	32.2 ± 9.4	31.8 ± 8.6	12.8 ± 3.9	23.2 ± 5.9	18.8 ± 21.8	7.3 ± 11.4	0	7.3 ± 11.4	7.8 ± 18.2	5.0 ± 12.2	61.2 ± 18.8

a. The unique Ni species in each sample, identified by XANES LCF are found in the ESI.

b. XANES results are for 11 samples only. M12 is not included.

c. XANES results are for 3 samples only. For samples M13 – M15, % contributions were unable to be determined.

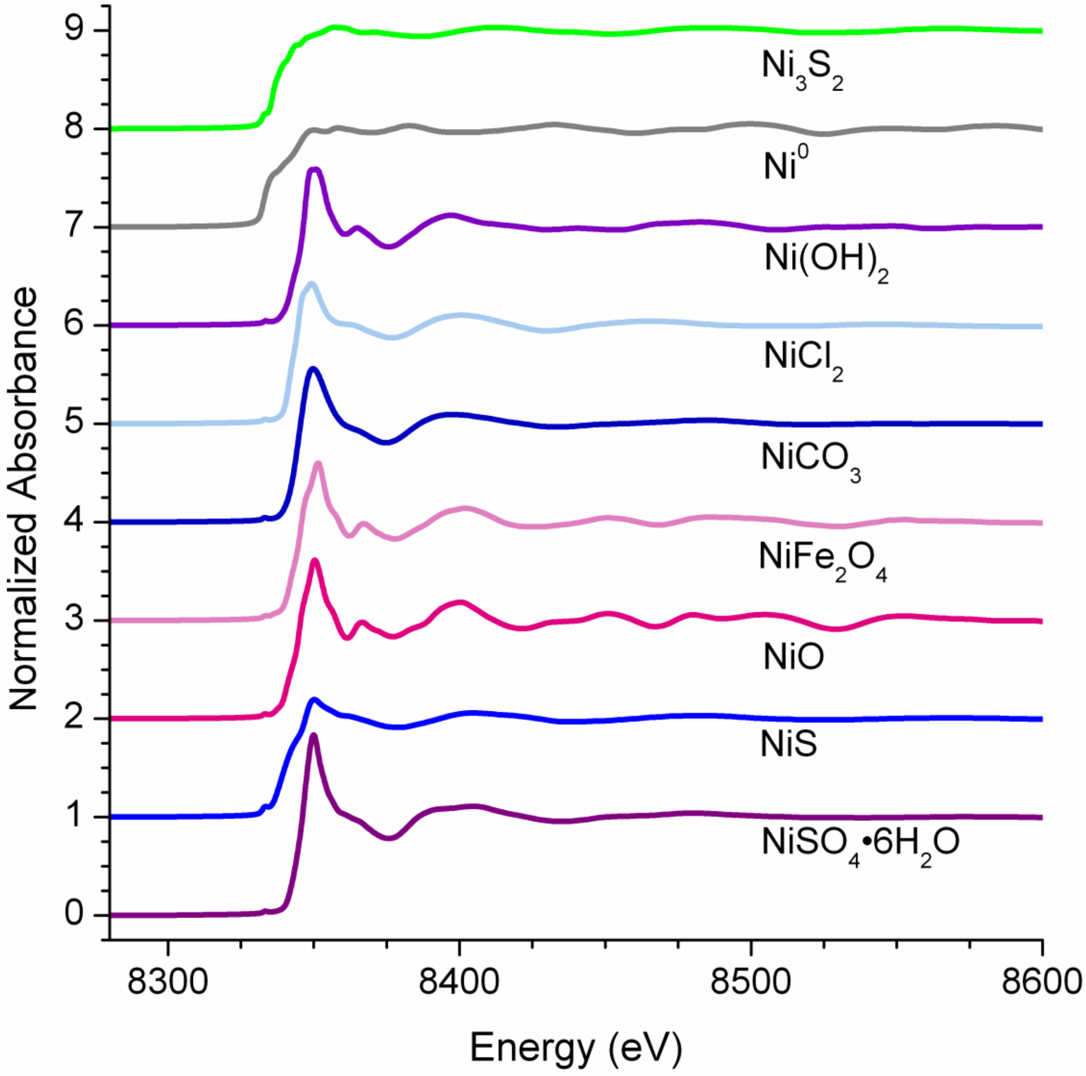

Figure 1. Nickel K-edge XANES reference compound spectra.

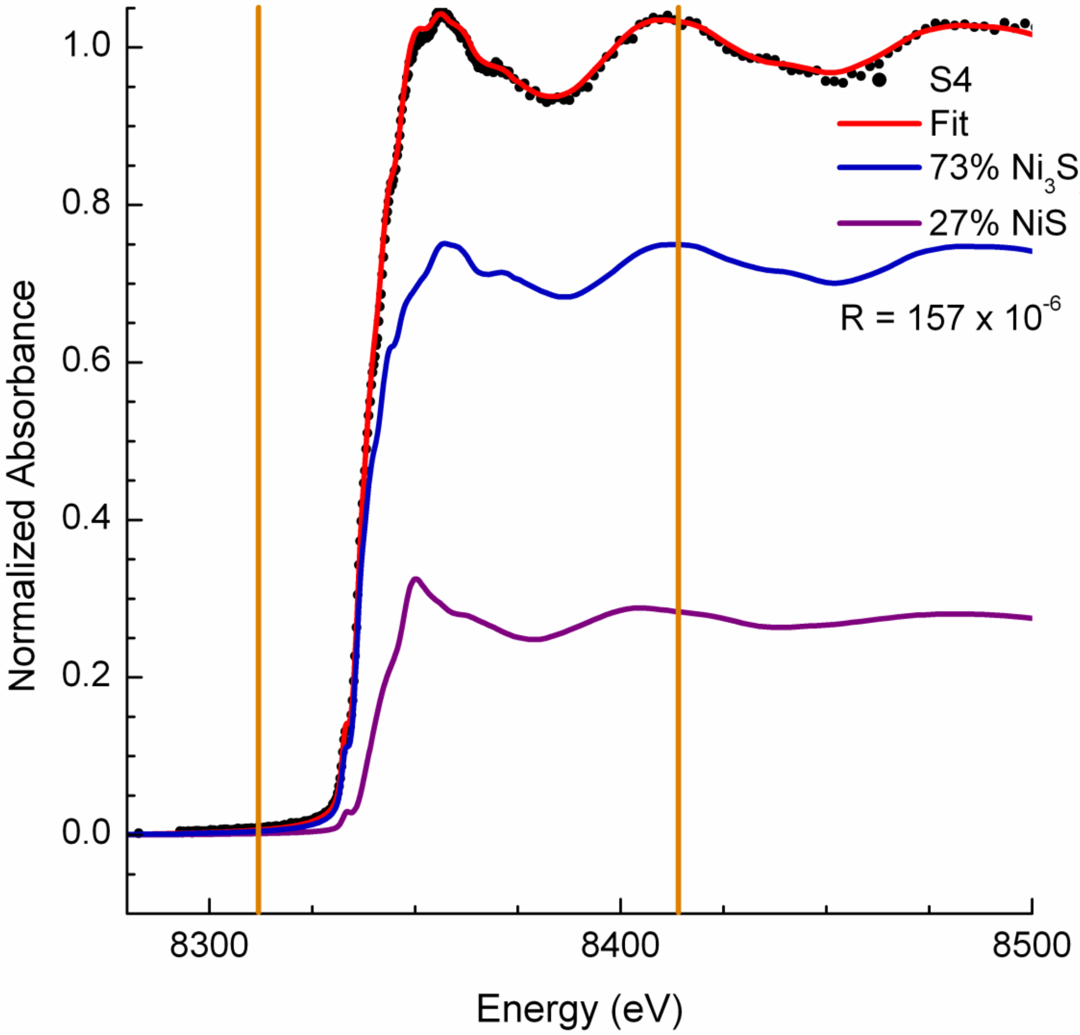

Figure 2. Nickel K-edge XANES spectrum of Sulphidic sample S4 is shown as black dots. The LC fit is shown in red. The component spectra of Ni_3S_2 and NiS are shown in blue and purple respectively. The orange bars indicate the LC fitting range.

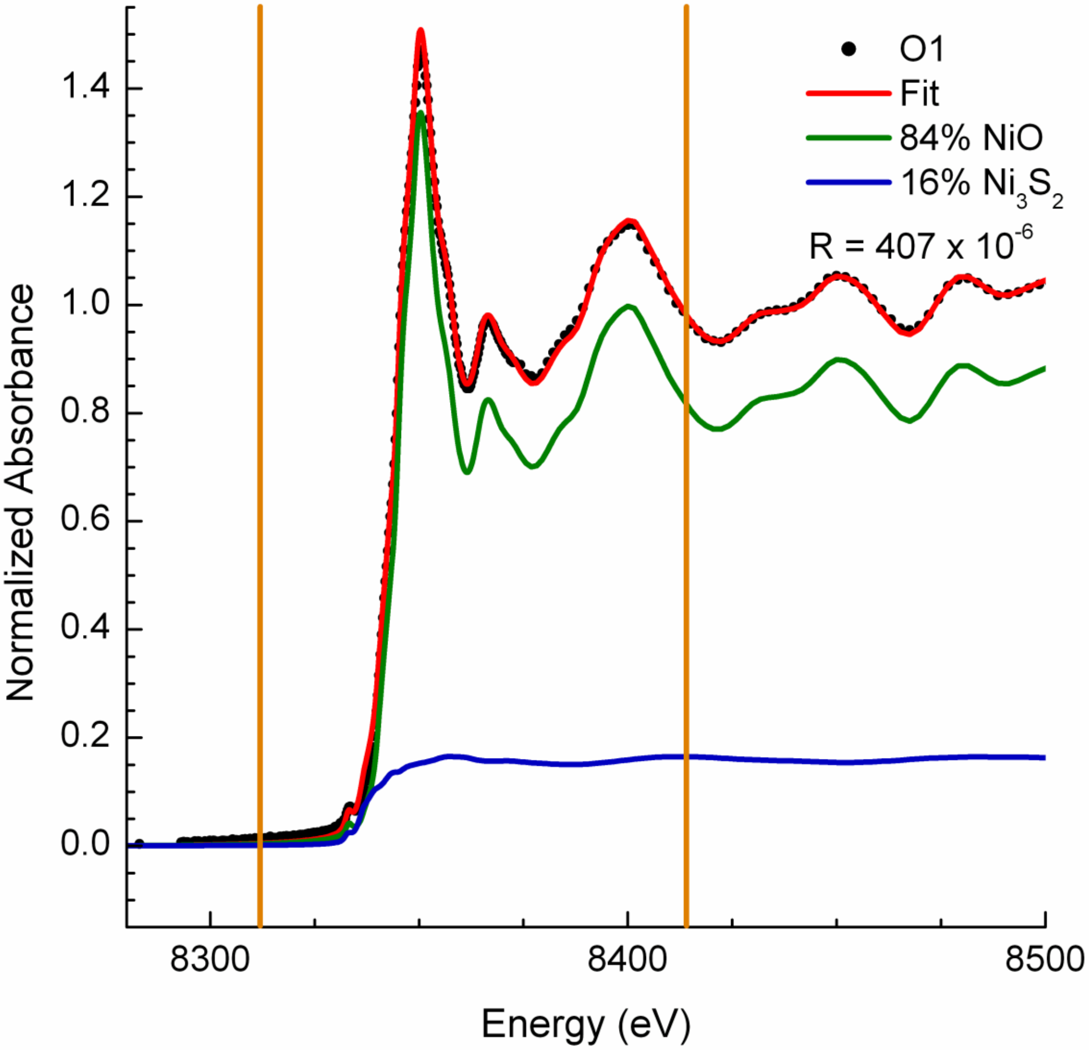

Figure 3. Nickel K-edge XANES spectrum of Oxidic sample O1 is shown as black dots. The LC fit is shown in red. The component spectra of NiO and Ni_3S_2 are shown in green and blue respectively. The orange bars indicate the LC fitting range.

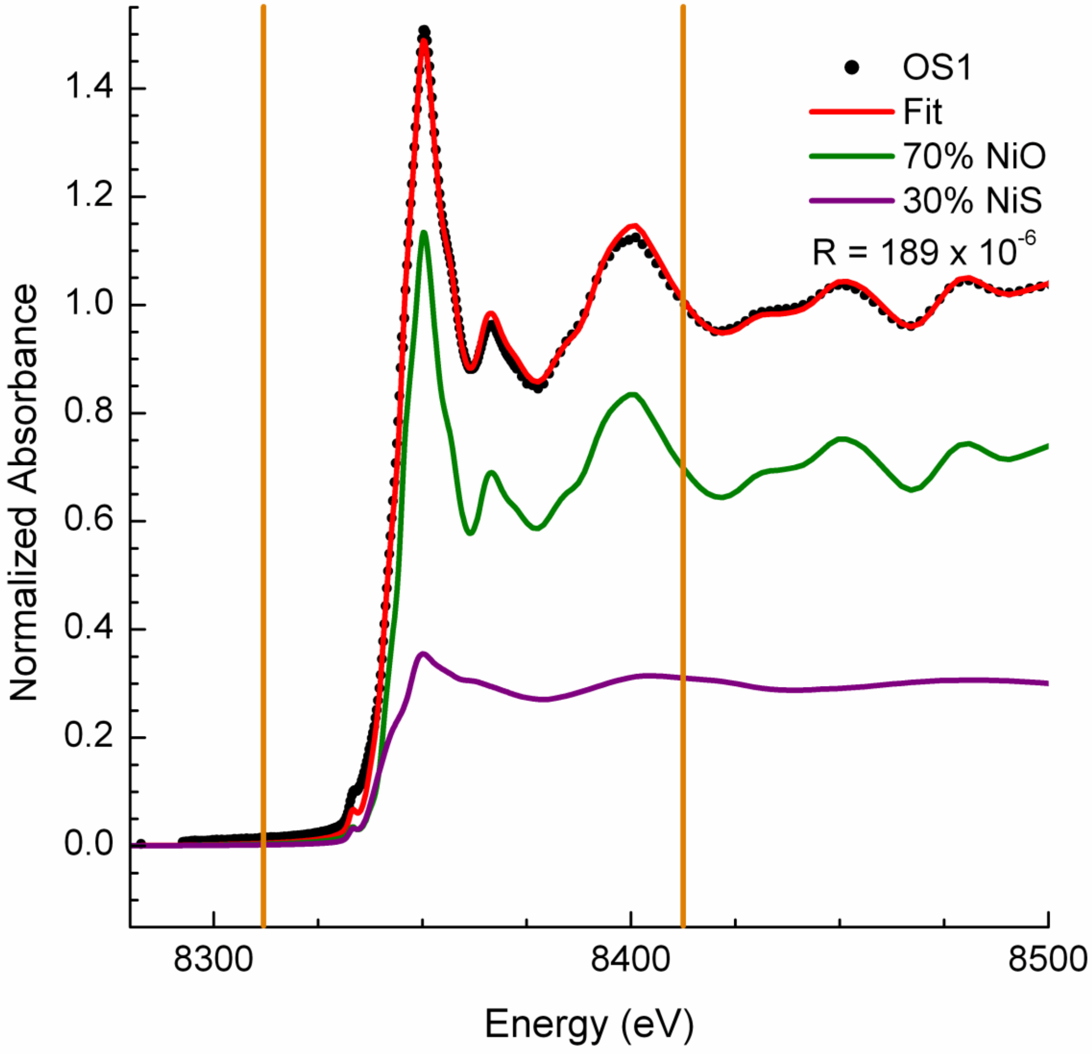

Figure 4. Nickel K-edge XANES spectrum of Oxidic/Sulphidic sample OS1 is shown as black dots. The LC fit is shown in red. The component spectra of NiO and NiS are shown in green and purple respectively. The orange bars indicate the LC fitting range.

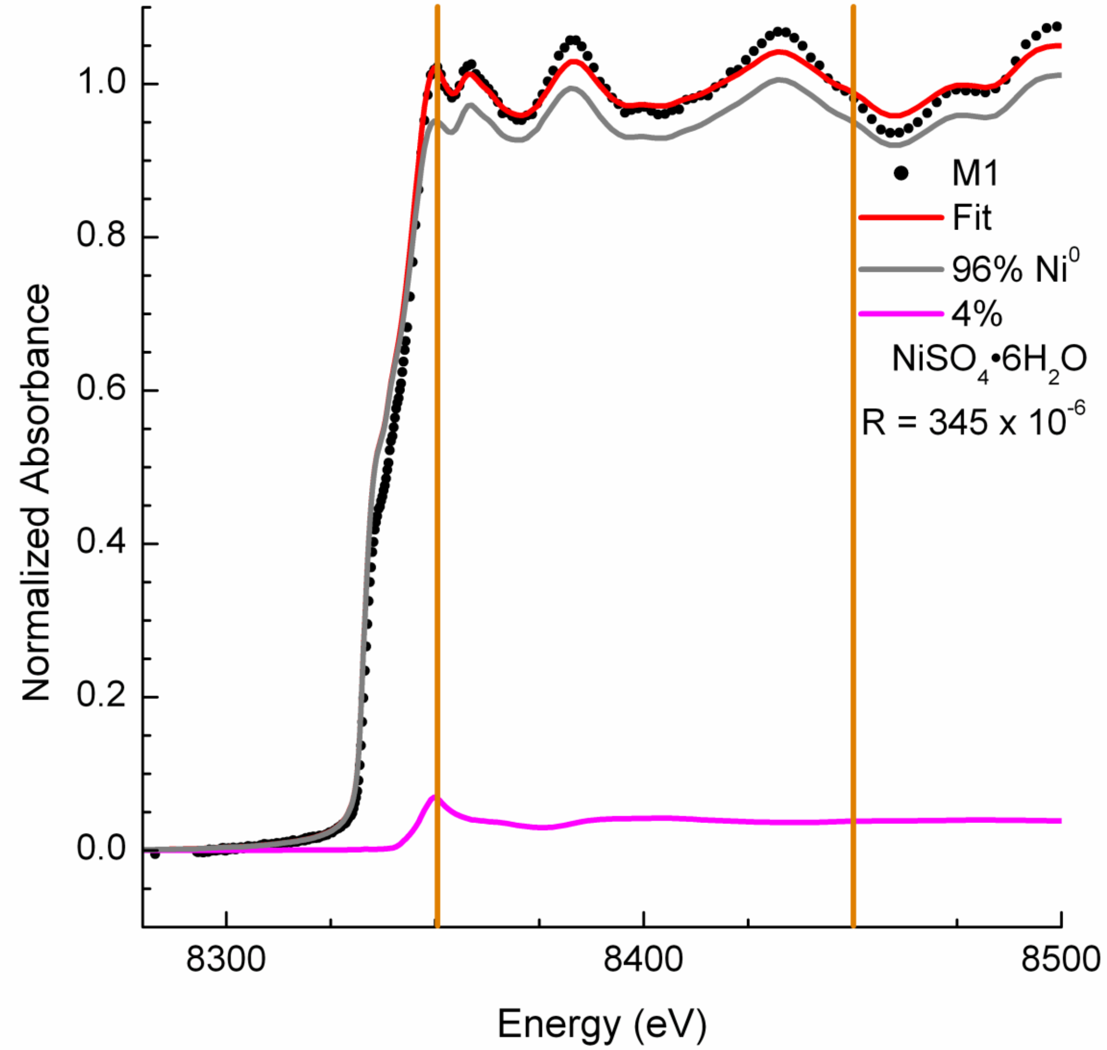

Figure 5. Nickel K-edge XANES spectrum of Metallic sample M1 is shown as black dots. The LC fit is shown in red. The component spectra of Ni^0 and NiSO$_4$ are shown in grey and pink respectively. The orange bars indicate the LC fitting range.

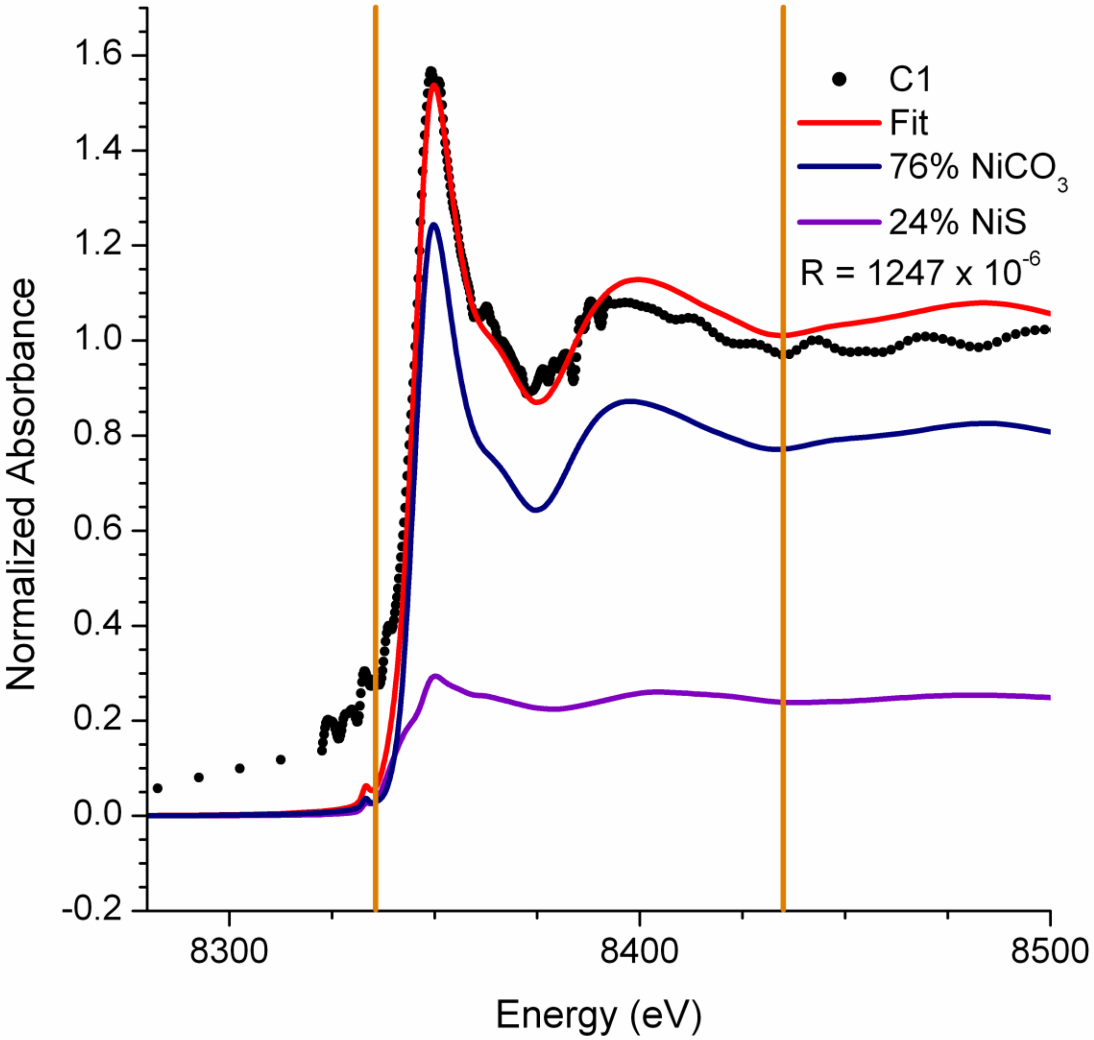

Figure 6. Nickel K-edge XANES spectrum of Carbonate sample C1 is shown as black dots. The LC fit is shown in red. The component spectra of $NiCO_3$ and NiS are shown in navy and purple respectively. The orange bars indicate the LC fitting range.

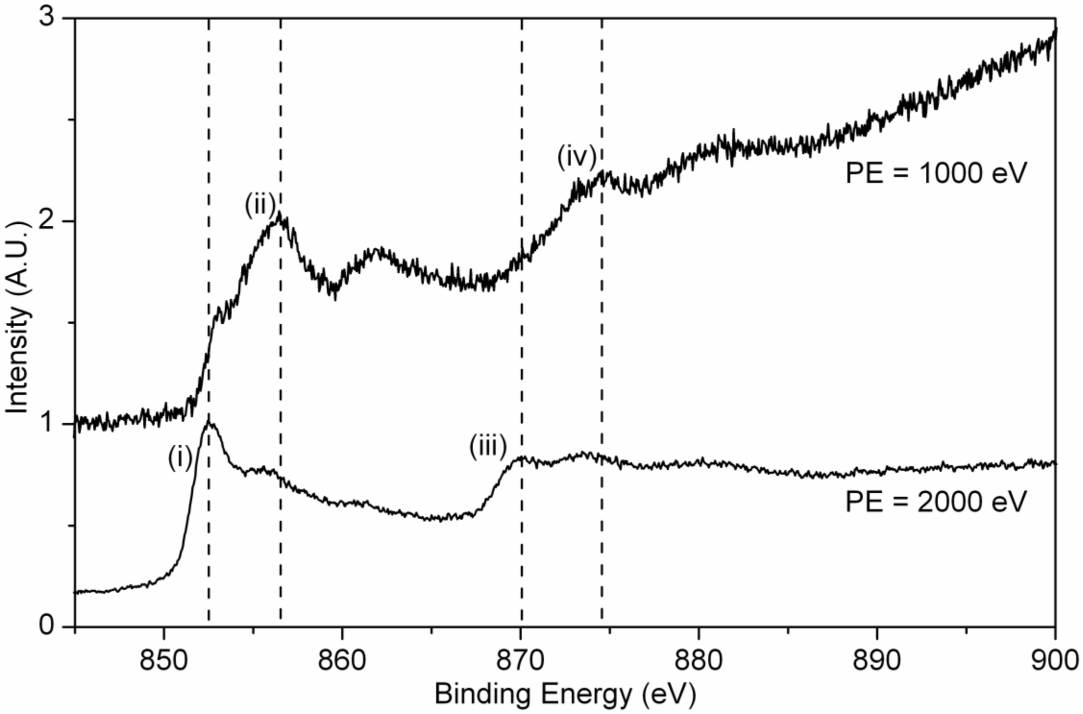

Figure 7. XPS spectra of Ni^0 nanopowder at two different photon energies: (upper spectrum) 1000 eV and (lower spectrum) 2000 eV. The intensities were normalized to the first major peak in each spectrum ((i) and (ii)).The dotted lines are guides for the eye. Spectral features to note are peaks at (i) 852.5 eV assigned to Ni, (ii) 856.4 eV assigned to Ni_2O_3, (iii) 870 eV assigned to NiO, and (iv) 874.6 eV assigned to Ni_2O_3.