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Mass Spectrometry & Spectroscopy

Nickel Bio-Monitoring in Human Urine by HR-CS AAS Using Novel Background Correction Routines

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Analytik Jena AG and Currenta GmbH & Co OHG have recently teamed-up to realise a fast urine screening routine for nickel that meets modern analytical requirements. Their objective was to develop a method that allows determining nickel contents from 4 to 50µg L^{-1} (ppb) with excellent precision and reliability of data for high-sample throughputs.

HR-CS AAS: contrAA® 700

Nickel which is ubiquitous in many industrial products including steel, coinage, batteries and jewellery was the contact allergen of the year 2008 since it causes severe dermatitis. Yet, nickel further exhibits carcinogenic potential when absorbed through inhalation as in case of workers in heavy metal industries. Besides, oral nickel intake especially from soy and cacao products, nuts and tea as well as tobacco consumption contributes to high human nickel exposure.

The overall nickel intake can be derived from the nickel content in urine, which is typically analysed by atomic absorption spectroscopy (AAS) [1]. Urine samples from people with occasional nickel exposure show contents of less than 3µgL^{-1}, while levels greater than 45µgL^{-1} are considered harmful, i.e. potentially carcinogenic [2].

When analysing human urine samples, dealing with spectral interferences from constituents of the urine matrix (e.g. phosphates) often influences the limit of analytical determination (sensitivity), the robustness of the method as well as its degree of automation.

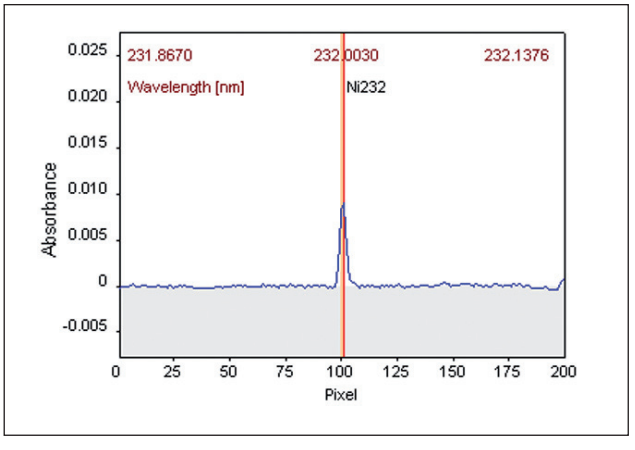

Figure 1. Atomic absorption spectrum of an aqueous 10µgL^{-1} (ppb) nickel standard collected on contrAA® 700 in the range from 231.8670 to 232.1376nm.

Here, the introduction of the high-resolution continuum source (HR-CS) AAS technology by Analytik Jena has opened a new avenue towards the realisation of screening methods for low trace metal contents in biological matrices. That is, unique spectral visualisation and integrated background correction routines allow for the powerful elimination of spectral interferences, and hence convenient method development.

Method development commenced with optimisation of the pyrolysis and atomisation temperatures for an aqueous 10 ppb Ni-standard using a furnace program comprising of three slow drying steps up to 110°C, two pyrolysis-, the atomisation as well as a cleaning step. A typical spectrum of the well-resolved 232.0nm Ni-AA-line analysed along with its immediate spectral environment is given in *Figure 1*.

When evaluating the integrated absorbance at 232.0nm as a function of pyrolysis and atomisation temperatures *(Figure 2)*, it was found that 950 and 2400°C were the best temperatures for the pyrolysis and atomisation step, respectively.

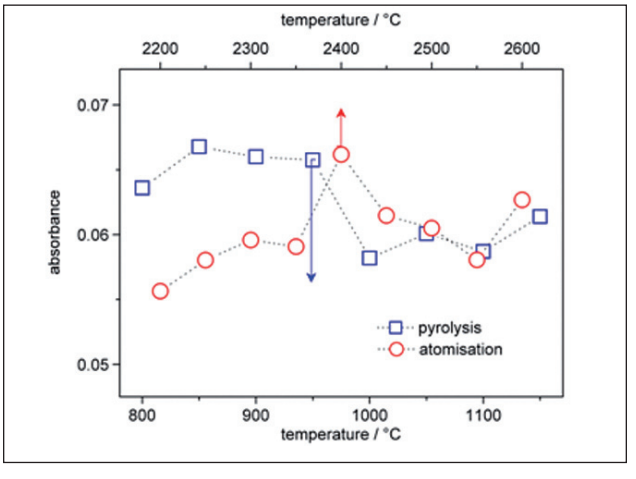

Figure 2. Absorbance for the Ni-AA-line at 232.0nm in dependence of pyrolysis and atomisation temperature.

From comparison of the spectra of the Ni-standard, the synthetic- as well as the human urine it became clear, that synthetic urine (recipe) was unsuitable for method development and calibration. The recipe spectrum was alike that of the nickel standard *(Figure 1)*, while the set of 3D-spectra for the human urine gave evidence for the presence of molecular absorptions (*Figure 3*, TOP PANEL) that were identified as phosphates and silicates using the in-built line-library. Those molecular absorptions arise from matrix constituents of human urine samples and directly overlap with the 232.0nm Ni-AA-line. Direct insight into such interferences simplifies required spectral correction routines and further benefits lower limits of analytical determination (sensitivity).

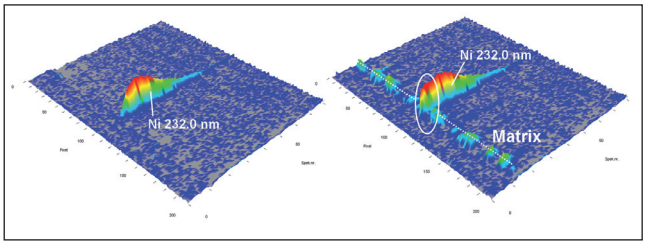

Figure 3. Set of 3D-spectra for the Ni-AA-line at 232.0nm as-collected on contrAA® 700 during the atomisation of human urine sample S 02 (top). Same set of 3D-spectra after spectral background correction of PO and SiO molecular absorptions (bottom).

In other words, using recipe as calibration standard for the screening of human urine samples means that spectral interferences due to PO and SiO molecular absorptions systematically falsify results, i.e. their contributions (absorbance) are unaccounted for in the calibration standards. Moreover, using certified human urine samples as calibration standard will yield similar problems as matrix constituents may differ substantially in any two urine samples.

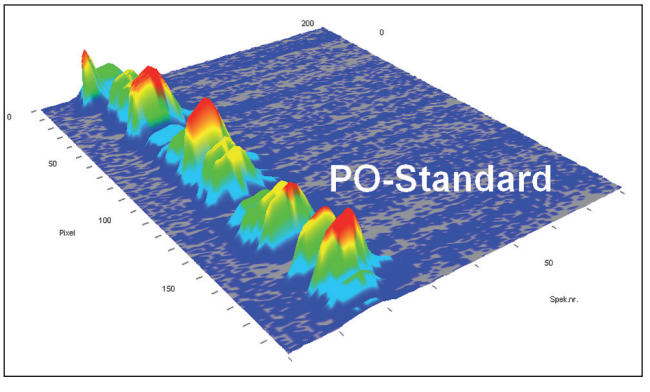

Figure 4. Set of 3D-spectra for a nickel-free sodium dihydrogenphosphate collected on contrAA® 700 for the wavelength range of the 232.0nm Ni-AA-line.

In order to develop a reliable screening method, the best approach to deal with spectral interferences is to correct/subtract false contributions using suitable correction spectra. In this study, sets of correction spectra were obtained from ultra-pure sodium dihydrogenphosphate *(Figure 4)* and sodium silicate *(Figure 5)* both of which were nickel-free.

These standards were chosen, because they produce the same spectral interferences found in the spectrum of human urine samples *(Figure 3, TOP PANEL)*. Using these correction spectra, a software-driven scaled subtraction routine developed by Analytik Jena can eliminate spectral interferences for human urine samples as evident in *Figure 3*, BOTTOM PANEL. Close inspection of both sets of 3D-spectra in *Figure 3* reveals that spectral contributions of the matrix constituents at 232.0 nm (Ni-AA-line) have been removed entirely.

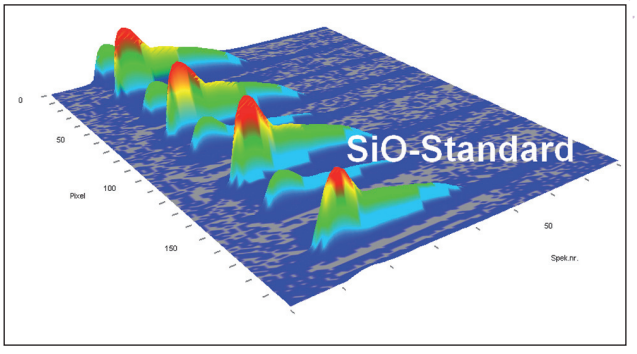

Figure 5. Set of 3D-spectra for a nickel-free sodium silicate collected on contrAA® 700 for the wavelength range of the 232.0nm Ni-AA-line.

The potential of this powerful background correction routine is best demonstrated when evaluating the results for the analysis of three human urine samples of known nickel contents (previously determined in a round robin test) denominated S 01, S 02 and S 03 *(see Table 1)*. Nickel contents from 4.5 to 36.7 ppb were chosen to account for the wide variety of human urine samples to be submitted to this screening routine.

Table 1. Comparison of nickel contents for three human urine samples analysed by electrothermal HR-CS AAS on contrAA® 700 with and without spectral background correction.

	nickel content in µg L^{-1}		
urine	determined		certified
sample	without correction model	with correction model	
S 01	15.4±0.8	5.3±0.3	4.5±1.2
S 02	19.6±0.1	10.4±0.2	9.9±2.1
S 03	44.9±0.7	36.9±0.2	36.7±6.6

For all three urine samples the nickel content determined by electrothermal HR-CS AAS were found to be in excellent agreement with certified nickel values; yet only when using the spectral background correction routines described above *(Table 1)*. That is, mean nickel contents for S 01, S 02 as well as S 03 were well within certified ranges when the background was properly corrected. On the contrary, when spectral interferences from PO and SiO constituents of human urine samples were unaccounted for in the analysis, nickel contents for S 01 and S 02 were over-estimated by about 300% and 200%, respectively.

It is worth noticing that the analytical routine developed at Currenta GmbH & Co OHG only involves the measurement of one aqueous blank and the urine sample as well as a 25 ppb spike for both of them. Considering the high accuracy and reproducibility of such approach it further safeguards the economic viability of a successful screening method.

References

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