



Determination of Total Nickel and Vanadium and Their Volatile and Thermally Stable Species in Crude Oil Using High-Resolution Continuum Source Graphite Furnace Atomic Absorption Spectrometry

Bernhard Welz

Department of Chemistry, Federal University of Santa Catarina (UFSC), Florianopolis, SC, Brazil • Email: welz@qmc.ufsc.br

Maria Goreti R. Vale

Institute of Chemistry, Federal University of Santa Catarina (UFSC), Florianopolis, SC, Brazil. • Email: mgrvale@ufrgs.br

The 'visibility' of the spectral vicinity of the analytical line at high resolution and the hitherto unattained performance of the truly simultaneous background correction are outstanding features of high-resolution continuum source atomic absorption spectrometry (HR-CS AAS). A potential source of error in the analysis of crude oil using graphite furnace AAS (GF AAS) was discovered with the aid of this technique. Part of the organic nickel and vanadium compounds (porphyrins) is volatile already at temperatures above 400°C and can be lost in the pyrolysis stage, whereas the salt-like, polar compounds of both elements are thermally stable up to 1300°C and 1600°C, respectively. HR-CS GF AAS also makes possible determining volatile and non-volatile species separately, which significantly increases the information content of the analyses.

The nickel and vanadium content found in crude oils is normally in the mg kg⁻¹ concentration range, i.e., in the 'upper trace' range. Both elements predominantly originate from the genesis of crude oil; their content provides information on the geographic origin of the crude oil and the relationship between the two elements is almost 'borehole-specific'. Nickel is a serious catalyst poison, which can cause undesired side reactions in the refining process. Breathable nickel dust and aerosols that are generated in the combustion of oil are considered to be carcinogenic. Vanadium leads to corrosion problems in combustion, especially in power stations. For these reasons, nickel and vanadium in crude oil and mineral oil products have to be determined routinely and reduced in concentration if necessary. GF AAS is one of the frequently used techniques for the determination of these two elements, as both of them are considered thermally stable, permitting high pyrolysis temperatures, which make possible straightforward separation of the complex oil matrix from the analytes – at least according to the established opinion.

Determination of nickel in crude oil using line source AAS

Figure 1 shows typical pyrolysis curves for nickel in a crude oil sample and a metal-organic standard, both in an oil-in-water emulsion to simplify pipetting. The measurements were recorded with conventional line source AAS (LS AAS) equipment and deuterium background correction (Analytik Jena Model AAS 5 EA). Everything seemed to be normal at a first glance, i.e., the nickel in the sample and in the standard was thermally stable up to around 1300°C, which agrees with expectations. The slight rise in the integrated absorbance values for the oil sample at pyrolysis temperatures lower than 1000°C was explained with incompletely corrected background absorption, which, however, was not considered a problem, as nickel was considered to be stable up to 1300°C anyway. This explanation firstly appeared plausible, as crude oil is an extremely complex matrix, often with a considerable content of non-volatile asphaltenes and resins, and the background absorption clearly exceeded the limits that could be corrected with the systems available for LS AAS when pyrolysis temperatures of less than 600°C were used.

Figure 1 Pyrolysis curves for nickel in a crude oil sample (—●—) and in a metal-organic nickel standard (—■—).

Determination of nickel in crude oil with HR-CS AAS

The introduction of instrumentation for HR-CS AAS [1,2] in the first decade of this century, finally, provided us with the means of studying this phenomenon of non-correctable background absorption in more detail. Particularly the highly resolved representation of the spectral vicinity of the analytical line and the extremely efficient simultaneous background correction of this technique offer completely new possibilities for GF AAS. Figure 2 shows the time- and wavelength-resolved absorption spectrum for a crude oil sample in the vicinity of the nickel line at 232.003 nm using a pyrolysis temperature of 600°C, i.e., under conditions where the suspected 'non-correctable background absorption' should arise. The spectrum, however, only shows the main resonance line and a secondary absorption line at 232.138 nm, which is also due to nickel, but no background absorption whatsoever that could be classified as 'non-correctable'. In addition, the pyrolysis curve recorded with HR-CS AAS also showed the same increase in integrated absorbance as with LS AAS (Figure 1) when pyrolysis temperatures lower than 1000°C were used.

This was a clear indication that the increase in integrated absorbance could not be due to a spectral problem, but was rather a real increase in sensitivity – an unambiguous reference to

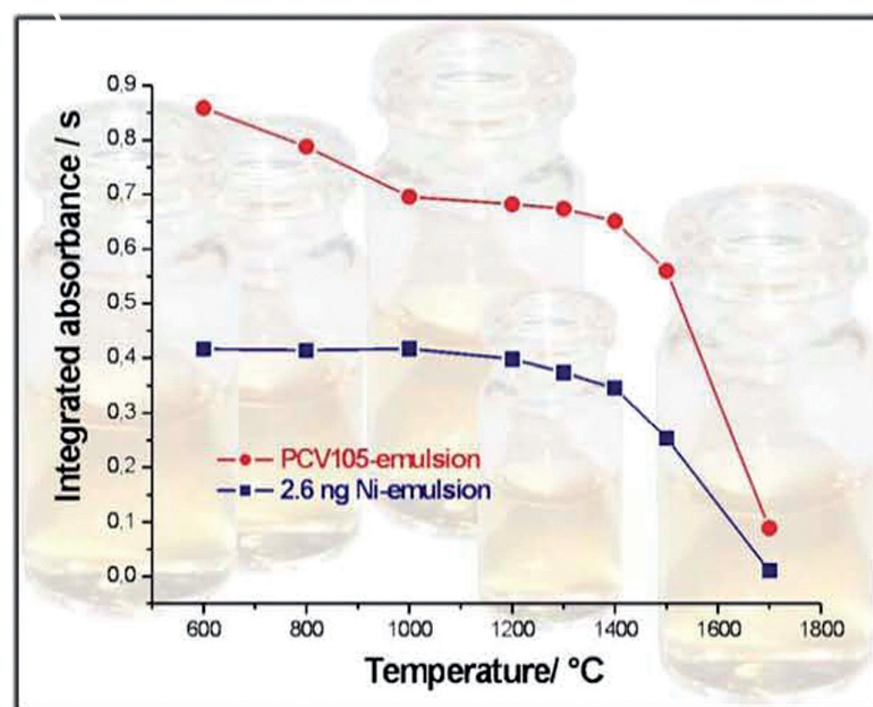


Figure 1: Pyrolysis curves for nickel in a crude oil sample (—●—) and in a metal-organic nickel standard (—■—)

analyte losses in this temperature interval. The logical decision was to go to even lower pyrolysis temperatures, which is possible without problems with HR-CS AAS due to the extremely efficient simultaneous background correction. Figure 3 shows the raw, uncorrected signal and the corrected absorbance signal for nickel in a crude oil sample measured at the center pixel at 232.003 nm and using a pyrolysis temperature of only 300°C.

The background absorption reached values of more than $A = 3$ under these conditions, an insoluble task for conventional background correction systems,

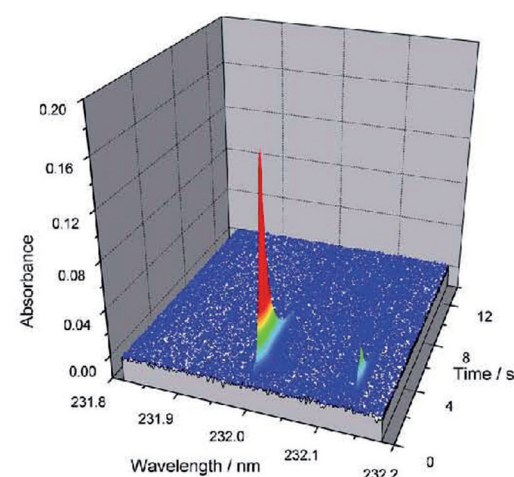


Figure 2: Time- and wavelength-resolved absorption spectrum for a crude oil sample in the vicinity of the nickel line at 232.003 nm; pyrolysis temperature 600°C, atomisation temperature 2500°C.

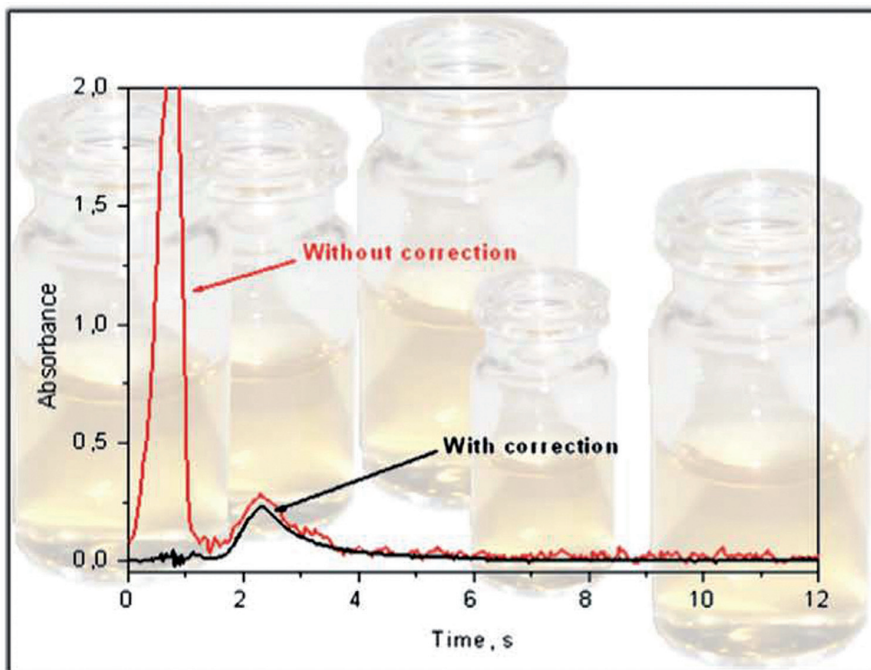


Figure 3: Time-resolved absorbance signals for Ni in a crude oil sample recorded at the center pixel at 232.003 nm; pyrolysis temperature 300°C, atomisation temperature 2500°C; Red signal: without background correction; Black signal: with automatic background correction

especially with the very rapidly changing background. Such background absorption is, however, no problem for HR-CS AAS, as measurement and correction take place strictly simultaneously and only a slight increase in the baseline noise is observed. The analyte signal is completely undistorted and can be evaluated without problems.

The pyrolysis curves for nickel [3,4] and vanadium [4,5] in crude oil recorded with HR-CS GF AAS are shown in Figure 4. It is quite apparent that considerable analyte losses occur for both elements at pyrolysis temperatures above 400°C. The existence of volatile compounds, especially nickel and vanadyl porphyrins, has indeed been described in the literature, but analyte losses in the pyrolysis stage of GF AAS have not been reported previously for these two analytes.

Speciation analysis using HR-CS GF AAS

HR-CS AAS makes possible quantitative determinations even with pyrolysis temperatures as low as 300°C, guaranteeing loss-free determination of total nickel and vanadium in crude oil. In addition, however, it also allows the determination of the thermally stable components, using a pyrolysis temperature around 1000°C, and calculating the content of volatile components (porphyrins) from the difference; it is only necessary to optimise the pyrolysis temperature accordingly. Table 1 shows some results of these 'speciation analyses' in a series of Brazilian crude oil samples and two reference materials. Table 1 shows that (1) the analyte content can vary by more than four orders of magnitude depending on the origin of the crude oil sample; (2) the volatile components can make up to 50% of the total content; and (3) the two reference materials that are commercially available, are not very well suited to render the analyte losses apparent, as the content of volatile compounds in both materials is very low.

Conclusion

Using HR-CS GF AAS it was possible revealing a real analytical problem in the determination of nickel and vanadium in crude oil, and also to solve it. Moreover, HR-CS GF AAS offers the possibility of also determining the content of volatile compounds of both elements in addition to the total content. This appears to be of particular importance, as the volatile compounds are

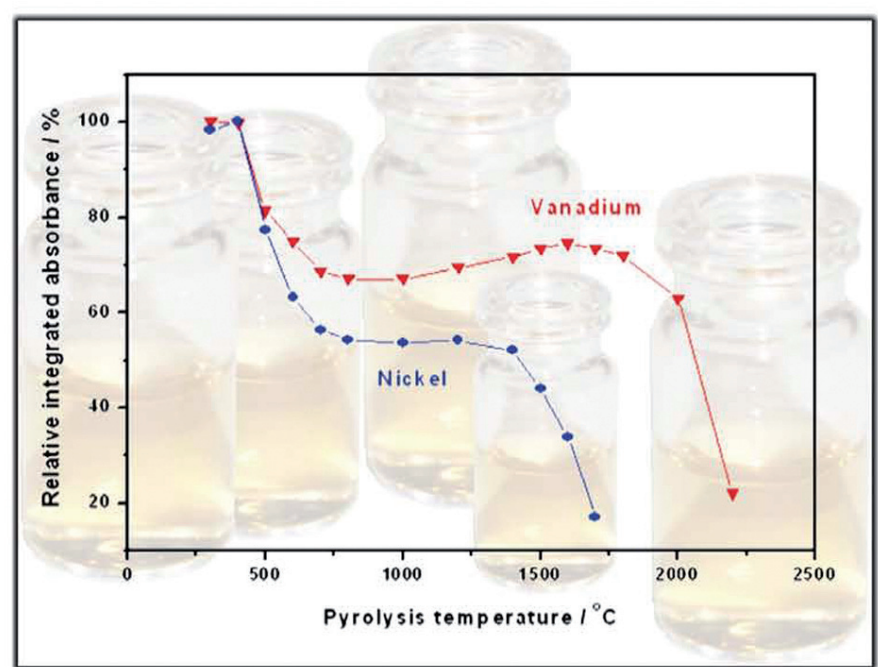


Figure 4: Pyrolysis curves for nickel and vanadium in a crude oil sample measured with HR-CS GF AAS

certainly transported preferentially in the distillation process to fractions such as naphtha and petroleum condensate, which are of particular industrial importance.

Finally it is worthwhile mentioning that probably most of the previously reported values for nickel and vanadium in crude oil determined with GF AAS were too low, i.e., wrong, as they only recorded data for the thermally stable components of these elements. Unfortunately, 'validation' with reference materials was hardly in a position to identify this error, as the few available materials contain almost exclusively non-volatile components.

Literature

- 1) B. Welz, H. Becker-Ross, S. Florek, U. Heitmann, High-Resolution Continuum Source AAS – The Better Way to Do Atomic Absorption Spectrometry, ISBN 3-527-30736-2, Wiley-VCH, Weinheim, 2005
- 2) B. Welz: High-resolution continuum source AAS – the better way to perform atomic absorption spectrometry, Anal. Bioanal. Chem. 381 (2005) 69-71.
- 3) M.G.R. Vale, I.C.F. Damin, A. Klassen, M.M. Silva, B. Welz, A.F. Silva, F.G. Lepri, D.L.G. Borges, U. Heitmann: Method development for the determination of nickel in petroleum using line-source and high-resolution continuum source graphite furnace atomic absorption spectrometry, Microchem. J. 77 (2004) 131-140.
- 4) I.C.F. Damin, M.G.R. Vale, M.M. Silva, B. Welz, F.G. Lepri, W.N.L. dos Santos, S.L.C. Ferreira: Palladium as a chemical modifier for the stabilization of volatile nickel and vanadium compounds in crude oil using graphite furnace atomic absorption spectrometry, J. Anal. At. Spectrom. 20 (2005) 1332-1336.
- 5) F.G. Lepri, B. Welz, D.L.G. Borges, A.F. Silva, M.G.R. Vale, U. Heitmann: Speciation analysis of volatile and non-volatile vanadium compounds in Brazilian crude oils using high-resolution continuum source graphite furnace atomic absorption spectrometry, Anal. Chim. Acta 558 (2006) 195-200.

Table 1: Determination of total, volatile and thermally stable nickel and vanadium species in various Brazilian crude oil samples and reference materials using HR-CS GF AAS. The total contents were measured using a pyrolysis temperature of 400 °C; the thermally stable components with a pyrolysis temperature of 1000°C, and the volatile components fraction was calculated from the difference.

Analyte →	Nickel			Vanadium		
	Total content mg kg ⁻¹	Thermally stable mg kg ⁻¹	Volatile fraction %	Total content mg kg ⁻¹	Thermally stable mg kg ⁻¹	Volatile fraction %
RM 8505 ^a	-	-	-	404 ± 6	402 ± 10	n.s. ^c
SRM 1634c ^b	17.4 ± 0.3	17.1 ± 1.1	n.s. ^c	29.0 ± 1.2	25.6 ± 1.3	12
OB 1	2.8 ± 0.1	2.1 ± 0.1	25	4.58 ± 0.18	2.26 ± 0.20	51
OB 2	21.8 ± 0.5	18.9 ± 0.2	13	30.1 ± 0.6	18.5 ± 0.7	39
OB 3	5.3 ± 0.4	3.5 ± 0.1	34	3.29 ± 0.10	2.28 ± 0.22	31
OB 4	1.3 ± 0.1	0.7 ± 0.1	46	0.23 ± 0.06	0.16 ± 0.05	30
OB 5	34.5 ± 1.6	25.6 ± 0.9	26	12.2 ± 0.3	8.8 ± 0.4	28
OB 6	34.0 ± 2.1	24.2 ± 0.7	29	8.75 ± 0.28	6.91 ± 0.40	21
OB 7	2.9 ± 0.5	2.4 ± 0.1	17	< 0.04	< 0.04	n.s. ^c

a - NIST RM 8505 vanadium in crude oil; recommended content: 390 ± 10 mg kg⁻¹ V; no value given for Ni

b - NIST SRM 1634c trace elements in fuel oil; certified: 17.5 ± 0.21 mg kg⁻¹ Ni; 28.19 ± 0.40 mg kg⁻¹ V.

c - n.s. = not significant; volatile component cannot be calculated, as no statistically significant difference exists between total and thermally stable content.