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Exploring potentialities of the HR-CS FAAS technique in the determination of Ni and Pb in mineral waters

*V. R.. Amorim Filho, V. P. Franzini, J. A. Gomes Neto**
[1]*Departamento de Química Analítica, Instituto de Química, Universidade Estadual Paulista, P.O. Box 355, 14801-970*
Araraquara - SP, Brazil
** anchieta@iq.unesp.br*

Abstract: National Health Surveillance Agency (ANVISA) established in the decree number 54 maximum allowed levels for Ni and Pb in mineral and natural waters at 20 µg L^{-1} and 10 µg L^{-1}, respectively. For screening analysis purposes, the high-resolution continuum source flame atomic absorption spectrometry technique (HR-CS FAAS) was evaluated for the fast-sequential determination of nickel and lead in mineral waters.Two atomic lines for Ni (232.003 nm – main and 341.477 nm – secondary) and Pb (217.0005 nm – main and 283.306 nm - secondary) at different wavelength integrated absorbance (number of pixels) were evaluated. Sensitivity enhanced with the increase of the number of pixels and with the summation of the atomic lines absorbances. The main figures of merit associated to the HR-CS FAAS technique were compared with that obtained by line-source flame atomic absorption spectrometry (LS FAAS). Water samples were pre-concentrated about 5-fold by evaporation before analysis. Recoveries of Pb significantly varied with increased wavelength integrated absorbance. Better recoveries (92-93%) were observed for higher number of pixels at the main line or summating the atomic lines (90-92%). This influence was irrelevant for Ni, and recoveries in the 92-104% range were obtained in all situations.

Keywords: Ni; Pb; mineral water; HR-CS FAAS; screening analysis.

Introduction

Drinking water is one of the main sources of contamination for humans and animals by toxic metals due to the large consumption [1,2]. The accurate determination of inorganic contaminants is important to help in water quality analysis. The Codex Alimentarius (FAO/WHO) and National Health Surveillance Agency (ANVISA) have been established the maximum allowed level for Ni and Pb in natural mineral waters at 20 ?g L^{-1} and 10 ?g L^{-1}, respectively [3,4]. The accurate determination of both elements at these low levels usually requires sensitive analytical techniques, such as electrothermal atomic absorption spectrometry (ET AAS) [5-7] or inductively coupled plasma mass spectrometry (ICP MS) [8]. For less sensitive techniques such as flame atomic absorption spectrometry (FAAS) [9] and inductively coupled plasma optical emission spectrometry (ICP OES) [8] sample pre-treatment is necessary prior to the determination [9,10].

Recently, new possibilities come up for the inorganic elemental analysis with the introduction of the high-resolution atomic-absorption spectrometry. The first commercial flame atomic absorption spectrometer (Analytik Jena model contrAA 300) is equipped with a high-intensity xenon short-arc lamp as a continuum radiation source and a compact high-resolution double echelle monochromator and a charge-coupled device (CCD) array detector with a resolution of about 2 pm per pixel in the far ultraviolet range [11-14]. In a recent review, the main advantages of using this system were described [11]. Among them is the possibility of performing fast-sequential multi-element measurements as well as concomitant measurements of main and secondary atomic lines. This new system either allows the use of two different strategies to improve the sensitivity: a) summation of absorbance signals of main and secondary atomic lines resulting in a new calibration function and b) integration of the absorbance signal over the center pixel by including part of the line wings, which is the same of increasing the number of pixels.

This paper reports on the evaluation and application of the high-resolution continuum source flame atomic absorption spectrometry technique in the determination of Ni and Pb for water screening analysis. The influence of the nature of atomic line (main and secondary), the summation of absorbance at these lines and the variation of number of pixels on sensitivity, accuracy and precision was studied. The performance of the method was checked by addition/recovery tests in four natural mineral water samples. The main figures of merit obtained by HR-CS FAAS were compared with the LS AAS technique.

Experimental

Apparatus or Instrumentation

A contrAA 300 (Analytik Jena, Germany) high-resolution atomic absorption spectrometer equipped with a xenon short-arc lamp (XBO 301, 300 W, GLE, Berlin, Germany) [15] as a continuum radiation source was used throughout the work. Two atomic lines were tested for each element. For nickel these lines were 232.003 nm (main) and 341.477 nm (secondary). For lead were 217.0005 nm (main) and 283.306 nm (secondary). For both elements, four different wavelength integrated absorbance were evaluated: CP (1 pixel), CP ± 1 (3 pixels), CP ± 2 (5 pixels) and CP ± 3 (7 pixels). For comparative purposes analysis were also done by using a line source equipment, a PerkinElmer AAnalyst 100 flame atomic absorption spectrometer (Shelton, CT, USA) equipped with hollow-cathode lamps as radiation sources for Ni (Part number N305-0152, i = 25 mA; slit = 0.2 nm; $\lambda = 232.0$ nm) and Pb (Part number N305-0157, i = 10 mA; slit = 0.7 nm; $\lambda = 217.0$ nm) determination. An oxidizing air/acetylene flame (Air Liquide, Sertãozinho, Brazil) was used in both spectrometers for analyte atomization. In both instruments an aspiration rate of about 5 mL min^{-1} was used. Measurements of each analyte were carried out in triplicate. A heating block (Tecnal, TE 015-150, Piracicaba, Brazil) was used to evaporate water samples.

Reagents, analytical solutions and samples

High purity water obtained with a Millipore Rios 5 ™ reverse osmosis and a Millipore Milli-Q Academic ™ system (resistivity 18.2 MΩ cm) was used throughout the study.

For Ni and Pb analysis using the contrAA 300 and AAnalyst 100 spectrometers, analytical solutions (25 - 800 µg L^{-1} Ni; 50 - 1000 µg L^{-1} Pb) were daily prepared by appropriate dilution of the 1000 mg L^{-1} stock standard solutions (Normex ™, Carlo Erba, Italy). All analytical solutions and samples were acidified to 1% v/v HNO_3 from a 70% v/v HNO_3 solution (Spectrum, New Brunswick, NJ, USA) to avoid hydrolysis.

Four natural mineral water bottles were purchased at a local market in Araraquara city, São Paulo State, Brazil. Samples were evaporated for analyte preconcentration before analysis. Aliquots of 100 mL of samples were evaporated in a heating block at 130 ^{o}C for 3 h until *ca.* 20 mL. The same pre-treatment was adopted for water samples spiked with 20 µg L^{-1} Ni and 10 µg L^{-1} Pb, performing final Ni and Pb concentrations of 100 µg L^{-1} and 50 µg L^{-1}, respectively.

Results and discussion

The parameters slope and correlation coefficient of the calibration curve, characteristic mass, limits of detection and quantification and standard deviation related to the main line, secondary line and summation of lines (∑ lines) at different wavelength integrated absorbance (number of pixels) were described in Table 1 and 2 for Ni and Pb, respectively. Analysis of Table 1 reveals that the sensitivity (slope and characteristic mass) improved with increased number of pixels. It should be commented that the LOD relative to the main line of nickel (232.003 nm) decreased from 4.1 to 2.5 µg L^{-1} when the number of pixels was ranged from 1 to 7. The calculated LOD for the secondary line did not change significantly. In this situation, the strategy of summating absorbance to increase sensitivity was ineffective since the LOD varied from 4.1 to 3.2 µg L^{-1} Ni when the wavelength integrated absorbance varied from 1 to 7 pixels. It is interesting to emphasize that the stan-

Table 1. Figures of merit for Ni at different wavelengths and number of pixels. $\sum_{\text{lines}}$ means summation of absorbance signals for all studied atomic lines.

1 pixel (CP)

Atomic line (nm)	Slope / R	C_o (µg L^{-1})	LOD (µg L^{-1})	LOQ (µg L^{-1})	SD_{blank}
232.003	0.04369/ 0.99818	100.7	4.1	13.7	0.00006
341.477	0.00949 / 0.99935	463.6	12.6	42.0	0.00004
$\sum_{\text{lines}}$	0.05317 / 0.99886	82.7	4.1	13.6	0.00007

3 pixels (CP ± 1)

Atomic line (nm)	Slope / R	C_o (µg L^{-1})	LOD (µg L^{-1})	LOQ (µg L^{-1})	SD_{blank}
232.003	0.11488/ 0.99895	38.3	4.2	14.0	0.00016
341.477	0.02547/ 0.99937	172.7	10.6	35.3	0.00009
$\sum_{\text{lines}}$	0.14034 / 0.99931	31.3	3.9	13.1	0.00019

5 pixels (CP ± 2)

Atomic line (nm)	Slope / R	C_o (µg L^{-1})	LOD (µg L^{-1})	LOQ (µg L^{-1})	SD_{blank}
232.003	0.15372/ 0.99960	28.6	3.1	10.3	0.00016
341.477	0.03455 / 0.99928	127.3	11.3	37.7	0.00013
$\sum_{\text{lines}}$	0.18827 / 0.99960	23.4	3.3	10.9	0.00021

7 pixels (CP ± 3)

Atomic line (nm)	Slope / R	C_o (µg L^{-1})	LOD (µg L^{-1})	LOQ (µg L^{-1})	SD_{blank}
232.003	0.16781/ 0.99979	26.2	2.5	8.3	0.00014
341.477	0.03794 / 0.99870	116.0	13.4	44.7	0.00017
$\sum_{\text{lines}}$	0.20575 / 0.99966	21.4	3.2	10.7	0.00022

R = Correlation coefficient; C_o = characteristic concentration (0.0044 / slope); LOD = limit of detection (3 x SD_{blank} / B); LOQ = limit of quantification (10 x SD_{blank} / B); SD_{blank} = standard deviation for 10 measurements of blank.

Table 2. Figures of merit for Pb at different wavelengths and number of pixels. $\sum_{\text{lines}}$ means summation of absorbance signals for all studied atomic lines.

1 pixel (CP)

Atomic line (nm)	Slope / R	C_o (µg L^{-1})	LOD (µg L^{-1})	LOQ (µg L^{-1})	SD $_{\text{blank}}$
217.0005	0.01829 / 0.99921	240.6	23.6	78.7	0.00014
283.306	0.01142 / 0.99077	385.3	50.9	169.7	0.00019
$\sum_{\text{lines}}$	0.02937 / 0.99933	149.8	24.1	80.3	0.00024

3 pixels (CP ± 1)

Atomic line (nm)	Slope / R	C_o (µg L^{-1})	LOD (µg L^{-1})	LOQ (µg L^{-1})	SD $_{\text{blank}}$
217.0005	0.04940 / 0.99961	89.0	16.5	55.0	0.00027
283.306	0.02890 / 0.99971	152.0	40.2	134.0	0.00039
$\sum_{\text{lines}}$	0.07827 / 0.99967	56.2	18.1	60.3	0.00047

5 pixels (CP ± 2)

Atomic line (nm)	Slope / R	C_o (µg L^{-1})	LOD (µg L^{-1})	LOQ (µg L^{-1})	SD $_{\text{blank}}$
217.0005	0.06842 / 0.99942	64.3	16.3	54.3	0.00037
283.306	0.03910 / 0.99969	112.5	32.5	108.3	0.00042
$\sum_{\text{lines}}$	0.10752 / 0.99961	40.9	15.6	52.0	0.00056

7 pixels (CP ± 3)

Atomic line (nm)	Slope / R	C_o (µg L^{-1})	LOD (µg L^{-1})	LOQ (µg L^{-1})	SD $_{\text{blank}}$
217.0005	0.07619 / 0.99861	57.7	12.4	41.3	0.00031
283.306	0.04322 / 0.99956	101.8	23.1	77.0	0.00033
$\sum_{\text{lines}}$	0.11941 / 0.99911	36.8	11.4	37.9	0.00045

R = Correlation coefficient; C_o = characteristic concentration (0.0044 / slope); LOD = limit of detection (3 x SD $_{\text{blank}}$ / B); LOQ = limit of quantification (10 x SD $_{\text{blank}}$ / B); SD $_{\text{blank}}$ = standard deviation for 10 measurements of blank.

dard deviation ($SD\Sigma_{\text{blank}}$) used in the equation 3xSD$_{\text{blank}}$/slope to calculate the LOD associated to the $\sum$ lines was: $SD\Sigma_{\text{blank}} = (SD^2_{\lambda 1} + SD^2_{\lambda 2})^{1/2}$, where λ1 and λ2 were the studied wavelengths [16]. From Table 1 it is possible to verify that nickel can be directly quantified in natural waters using the main atomic line and 7 pixels at concentration until 8.3 µg L^{-1}, almost 2.4-fold lower than the maximum allowed level (20 µg L^{-1} Ni) in waters established by ANVISA. It should be mentioned that the calculated characteristic concentration (C_o) obtained with 3 pixels at the main line (38.3 µg L^{-1}) is close to that furnished by the manufacturer (40.0 µg L^{-1}). For comparison purposes, this characteristic concentration is almost 3.3-fold lower than that obtained by LS FAAS (126 µg L^{-1}) at the same wavelength. For the secondary atomic line and 5 pixels, the obtained C_o is 127.3 µg L^{-1}.

High concentrations of Fe or Cr in real samples may increase the Ni signal. Usually, interferences like that could be eliminated by the use of the N_2O/C_2H_2 flame, although the Ni sensitivity will be lower. Using the HR-CS FAAS technique a possibility to avoid this kind of interferences without losses in sensitivity will be to employ the secondary line and 5 pixels without the need of chang-

Table 3. Recoveries (in %) for Ni in spiked natural mineral waters obtained in all studied conditions.

1 pixel (CP)			
Sample	Recovery (%) **232.003 nm**	Recovery (%) **341.477 nm**	Recovery (%) Σ_{lines}
1	96	104	97
2	94	103	95
3	101	99	100
4	97	104	101
3 pixels (CP ± 1)			
Sample	Recovery (%) **232.003 nm**	Recovery (%) **341.477 nm**	Recovery (%) Σ_{lines}
1	96	104	99
2	98	94	96
3	97	94	95
4	99	98	97
5 pixels (CP ± 2)			
Sample	Recovery (%) **232.003 nm**	Recovery (%) **341.477 nm**	Recovery (%) Σ_{lines}
1	104	100	103
2	97	97	98
3	101	92	100
4	98	95	96
7 pixels (CP ± 3)			
Sample	Recovery (%) **232.003 nm**	Recovery (%) **341.477 nm**	Recovery (%) Σ_{lines}
1	99	95	98
2	103	94	96
3	97	91	93
4	98	90	94

ing the type of the atomization flame (oxidizing air/C_2H_2).

Shown in Table 2 are the main figures of merit for Pb at 217.0005 nm (main line) and 283.306 nm (secondary line) using different number of pixels. In contrast to line source AAS technique, where the main line (217.0 nm) exhibits a poor signal to noise ratio compared with the 283.0 nm atomic line resulting in a pronounced non-linearity and worse LOD values; in HR-CS

Table 4. Recoveries (in %) for Pb in spiked natural mineral waters obtained in all studies conditions.

1 pixel (CP)			
Sample	Recovery (%) **217.0005 nm**	Recovery (%) **283.306 nm**	Recovery (%) Σ_{lines}
1	85	80	84
2	87	81	83
3	82	81	81
4	84	80	83
3 pixels (CP ± 1)			
Sample	Recovery (%) **217.0005 nm**	Recovery (%) **283.306 nm**	Recovery (%) Σ_{lines}
1	88	82	86
2	86	84	85
3	84	84	84
4	89	83	86
5 pixels (CP ± 2)			
Sample	Recovery (%) **217.0005 nm**	Recovery (%) **283.306 nm**	Recovery (%) Σ_{lines}
1	90	86	88
2	89	87	88
3	91	88	90
4	90	85	87
7 pixels (CP ± 3)			
Sample	Recovery (%) **217.0005 nm**	Recovery (%) **283.306 nm**	Recovery (%) Σ_{lines}
1	92	85	90
2	93	87	92
3	92	85	91
4	93	88	92

AAS technique the main line can be used without problems due to the much higher radiation intensity available from the xenon short-arc lamp [17]. The characteristic concentration (C_o) obtained by HR-CS FAAS that more approximated with the manual value (73.0 µg L^{-1}) was 64.3 µg L^{-1} (5 pixels at 217.0005 nm). The experimental and manual C_o values using the LS FAAS technique were 192 and 190 µg L^{-1}, respectively. In relation to LOD values, the HR-CS FAAS presented results in the optimal situation (7 pixels at ∑ lines; LOD = 11.4 µg L^{-1}) *ca.* of 8-fold lower than that obtained by LS FAAS (92.0 µg L^{-1}). Limit of detection relative to the main line of Pb (217.0005 nm) decreased from 23.6 to 12.4 µg L^{-1} when the number of pixels was ranged from 1 to 7, while for the secondary line (283.306 nm) this value decreased from 50.9 to 23.1 µg L^{-1}. Although the strategy of summating absorbance to increase sensitivity was less effective for Ni changing the wavelength integrated absorbance from 1 to 7 pixels; for Pb the LOD values ranged from 24.1 to 11.4 µg L^{-1}.

Tables 3 and 4 present recovery percentages for Ni and Pb, respectively, for all studied conditions. Recoveries of Pb significantly varied with increased wavelength integrated absorbance. Better recoveries (92-93%) were observed for higher number of pixels at the main line or summating the atomic lines (90-92%). This influence was irrelevant for Ni, and recoveries in the 92-104% range were obtained in all situations.

Conclusions

The HR-CS FAAS technique showed to be promising in elemental analysis field when sub-ppm is required. In this work an evaluation of the potentialities of the HR-CS FAAS was done in the determination of Ni and Pb for water screening analysis. The increased number of pixels (wavelength absorbance integrated) and the summation of the absorbance signals of the main and secondary atomic lines were studied.

For Ni the LOD relative to the main line of nickel (232.003 nm) decreased from 4.1 to 2.5 µg L^{-1} when the number of pixels was ranged from 1 to 7. At the secondary atomic line this parameter did not change significantly.

For Pb the LOD relative to the main line of Pb (217.0005 nm) decreased from 23.6 to 12.4 µg L^{-1} when the number of pixels was ranged from 1 to 7, while for the secondary line (283.306 nm) this value decreased from 50.9 to 23.1 µg L^{-1}.

Although the strategy of summating absorbance to increase sensitivity was less effective for Ni changing the wavelength integrated absorbance from 1 to 7 pixels; for Pb the LOD values ranged from 24.1 to 11.4 µg L^{-1}.

Another advantage that should be mentioned is the reduction analysis time. All analyzed natural mineral water samples presented Ni and Pb levels lower than the maximum allowed level by the *Codex Alimentarius* and National Health Surveillance Agency (ANVISA).

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V. R. Amorim Filho, V. P. Franzini, J. A. Gomes Neto. Explorando potencialidades da técnica HR-CS FAAS na determinação de Ni e Pb em água mineral.

Resumo: De acordo com a Resolução nº 54 da Agência Nacional de Vigilância Sanitária (ANVISA), os limites máximos permitidos para níquel e chumbo em água mineral natural e água natural são 20 μg L^{-1} e 10 μg L^{-1}, respectivamente. O presente trabalho apresenta o potencial de uso da técnica de espectrometria de absorção atômica em chama com fonte contínua e de alta resolução (HR-CS FAAS) na determinação seqüencial rápida de níquel e chumbo para fins de análise classificatória de água mineral de acordo com a ANVISA. Duas linhas de absorção atômica foram empregadas para níquel (232,003 nm – principal e 341,477 nm – secundária) e chumbo (217,0005 nm - principal e 283,306 nm - secundária) e diferentes volumes de linha (número de pixels). Em geral, a sensibilidade melhorou com o aumento do número de pixels e com a soma das absorbâncias das linhas atômicas estudadas. As principais figuras de mérito obtidas com a técnica HR-CS FAAS foram comparadas com a espectrometria de absorção atômica em chama com fonte de linhas (LS FAAS). As amostras de água mineral foram evaporadas antes de serem analisadas de modo a obter um fator de pré-concentração de aproximadamente cinco vezes. As recuperações de Pb variaram significativamente com o aumento do volume das linhas. As melhores recuperações foram observadas na linha principal (92-93%) e na somatória de ambas (90-92%). No caso do Ni, esta influência foi pouco relevante, sendo que a recuperação variou de 92-104%.

Palavras-chave: Ni; Pb; água mineral; HR-CS FAAS; análise classificatória.

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