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Short communication

Determination of traces of Ni in Li_2CO_3/Na_2CO_3 melts by graphite furnace atomic absorption spectrometry

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Abstract

A graphite furnace atomic absorption method is described for the determination of traces of Ni in 52 mole percent (mol.%) Li_2CO_3 and 48 mol.% Na_2CO_3 melts after dissolution of the sample in dilute nitric acid. Maximum pyrolysis and optimum atomisation temperatures for the analyte were determined in the presence of the Li and Na matrix constituents. Pre-pyrolysed ascorbic acid (typical amount of 5 μg) has been used as chemical modifier for effectively suppressing the chemical and spectral interferences of the Li/Na matrix, thus that the analysis can be conducted using acid-matched standard solutions. The results of the Ni analysis in synthetic sample solutions by calibration graph against acid-matched standards well agree with those obtained by the method of standard additions. Recoveries ranged from 99 to 101% and the relative standard deviation is around 3% at the 20 $\mu g\,L^{-1}$ level. Moreover, the use of the chemical modifier leads to an improvement of the lifetime of the graphite tube. The Ni detection limit (3σ) in Li/Na carbonate melts for the proposed method is similar to that obtained in aqueous solution, i.e. 5×10^{-8} g analyte per gram of $(Li_{0.52}Na_{0.48})_2CO_3$ melt. This method is successfully applied to the determination of nickel in real carbonate melt samples.

Keywords: Nickel; Alkali metal carbonate melts; Graphite furnace atomic absorption spectrometry; Pre-pyrolysed ascorbic acid chemical modifier; Molten carbonate fuel cells

1. Introduction

The determination of trace levels of Ni in $(Li_{0.52}Na_{0.48})_2CO_3$ melts is of concern in the molten carbonates fuel cells (MCFCs) technology, because the slow dissolution of the NiO cathode in the electrolyte reduces the life-time of the cell [1,2]. Although it is felt that solubility data are needed for the NiO, the experimental details on solubility measurements are often lacking. In a previous work of the author, an optimised flame atomic absorption spectrometric method for the determination of traces of Ni, Co and Fe in $(Li_{0.62},K_{0.38})_2CO_3$ melts has been developed [3]. A detection limit of 0.5×10^{-6} g analyte per gram electrolyte has been obtained under the optimised conditions. However, the determination of lower Ni concentration in the $(Li_{0.52},Na_{0.48})_2CO_3$ melts requires the use of a more sensitive analytical technique.

Among spectroscopy techniques, graphite furnace atomic absorption spectrometry (GF AAS) allows to achieve the lowest detection limits, although the high contents of alkali elements in the sample may yield chemical and spectral interferences. It is well documented in the literature the effect of alkali metals on the analytical signal of the analyte in the graphite tube [4,5]. For accurate and precise measurements an optimised method has to be established in order to minimise matrix interferences. Matrix matched standards might be used in the analysis of metals in frozen molten salts if the exact composition of samples is known or the standard additions method even though it is time-consuming overall when several samples must be analysed. Therefore, it is necessary to knew the mechanism of the matrix interference on the analyte signal in order to effectively remove the major constituents by choosing the appropriate temperature of the

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pyrolysis stage or adding matrix modifier so that analyte lost during the thermal programs are minimised and a complete analyte atomisation takes place in the furnace.

In the present work a simple and reliable analytical method for the determination of traces of Ni in $(Li_{0.52}Na_{0.48})_2CO_3$ melts by GF AAS is described. The interference effects produced by the high levels of lithium and sodium on the absorbance signal of the analyte are markedly reduced by using ascorbic acid as chemical modifier. The detection limit, sensitivity, accuracy and precision are evaluated for Ni in Li/Na carbonate melts. The proposed method is applied to the solubility measurements of nickel based cathode materials in carbonate melts.

2. Experimental

2.1. Instrumentation

A Varian SpectrAA 220FS (Victoria, Australia) atomic absorption spectrometer equipped with a GTA110 graphite furnace, an auto-sampler and a deuterium lamp as background correction system was used. Hollow cathode lamp (Varian) of Ni was used as source. The instrumental parameters of the spectrophotometer were as follows: wavelength at 232.0 nm and bandpass 0.2 nm. Pyrolytic graphite-coated graphite tubes were used. Argon (99.999%) gas was fluxed in the graphite tube. Peak height absorbance signals were measured by the AA instrument. The temperature program for the graphite tube is reported in Table 1. The samples were weighted with an AND HM-202 microbalance with 0.001 μg accuracy. High-density polyethylene volumetric flasks and cups (Nalge Company, Rochester, NY, USA) were soaked in dilute nitric acid (3%) for 24 h and rinsed several times with deionised water before use. Eppendorf micropipettes were used to prepare solutions.

2.2. Reagents and standard solutions

Ultra-high-purity water with a specific resistance of 18.2 MΩ cm from a Milli-Q Gradient water purification system (Millipore S.A.S., Molshem, France) and filtered through a 0.22 μm membrane filter was used for all preparations and dilutions. All chemicals were of analytical-reagent grade. Standard solution of 35 μg L^{-1} Ni was daily prepared by making serial dilutions of a 1000 mg L^{-1} atomic absorption stock solution (Aldrich) with dilute nitric acid. Five working standard solutions were prepared with the auto-sampler by taking different volumes of the standard solution. The acidity of the standard solutions was matched to that of the sample solutions. Appropriate amounts of Li_2CO_3 and Na_2CO_3 (Merck, Suprapur grade, previously dried at 250 °C for 4 h) were dissolved in acidified water to make 0.25 mol L^{-1} Li and 0.16 mol L^{-1} Na solutions. Then these solutions were used to prepare the blank sample solution and the matrix-matched standards. A 0.1% (m/V) ascorbic acid (Merck) solution was prepared.

2.3. Decomposition of melts

Accurately weighed amounts of carbonate melts (52 mol.% Li_2CO_3 and 48 mol.% Na_2CO_3) between 0.8 and 1.2 g were transferred to 50 mL covered beakers and dissolved in 2 mL of concentrated HNO_3 by gentle heating and magnetic stirring on a hot plate. After cooling, the solutions were transferred to 50 mL clean volumetric flasks and made up to volume with deionised water. The sample solutions were analysed for the Ni content in three replicate runs. The gathered results were expressed as mole fraction of NiO in the melt.

2.4. Procedure

The optimised drying and pyrolysis temperature and holding time were chosen for nickel. Ni concentration was measured using ascorbic acid as chemical modifier. The modifier solution (5 μL) was injected before each cycle, dried and pyrolysed at the temperature of pyrolysis of nickel analyte, followed by injection of 10 μL of the sample solution. Alternatively, the modifier solution was co-injected to the sample solution.

3. Results and discussion

3.1. Optimisation of pyrolysis and atomisation temperature

The effect of pyrolysis and atomisation temperature on the analytical signal of 0.4 ng Ni both in aqueous and Li/Na solutions is shown in Fig. 1. The atomic signal for Ni diminished with pyrolysis temperature above 900 °C both in aqueous and matrix medium (Fig. 1a and b, respectively). The effect of atomisation temperature is almost constant on

Table 1
Heating program of the graphite furnace

Step	Dry			Pyrolysis			Atomisation		
	I	II	III	I	II	III	I	II	III
Temperature (°C)	85	95	120	800	800	800	2100	2100	2100
Hold time (s)	5.0	40.0	10.0	5.0	1.0	2.0	1.3	2.0	2.0
Gas flow rate (L min^{-1})	3.0	3.0	3.0	3.0	3.0	0.0	0.0	0.0	3.0

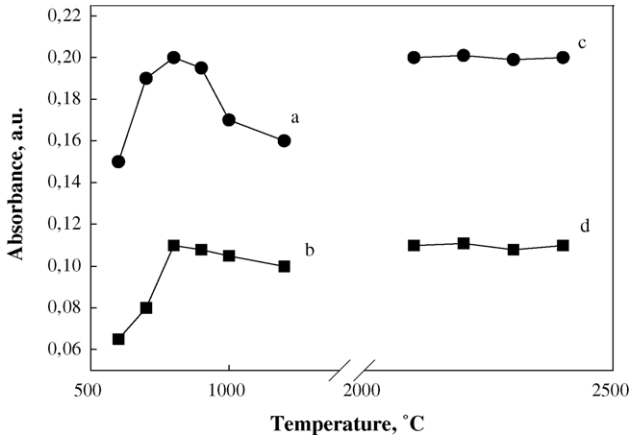

Fig. 1. Pyrolysis (a, b) and atomisation (c, d) curves of 0.4 ng Ni in both aqueous (●) and Li/Na (■) media. Temperature of atomisation of 2100 °C during pyrolysis step. Temperature of pyrolysis of 800 °C during atomisation step.

the Ni analytical signal in both matrices (Fig. 1c and d). The sensitivity of Ni atomic signal in presence of concomitants Li and Na is depressed by about 40% over a wide temperature range of the pyrolysis curves and depending on the number of runs. During decomposition of sample the major elements Li and Na are transformed to their corresponding nitrates, which decompose at low temperatures and are expected to volatilise in the pyrolysis step [6]. However, condensed phase interference occurs as indicated by an early non-atomic spectral band of Li/Na matrix partially overlapped in time to the atomic absorption signal of Ni (Fig. 2). Moreover, the absorbance of the non-atomic absorption of Li/Na matrix mostly depends on both the state of the pyrolytic-graphite coating graphite tube and the contamination level of residue matrix coming from the previous injections. It has been observed that high level of absorbance (above 1.0 absorptivity unit) can be reached with the increase of firings. It is well known that alkaline elements and metal oxides strongly interact with the walls of the graphite tube, as well HNO_3, which are then release during the atomisation step, leading to corrosion of the carbon planes [7,8].

3.2. Effect of the ascorbic acid chemical modifier

The effectiveness of organic acids on matrix modification has been extensively studied [9], therefore it has been here explored the use of ascorbic acid as matrix modifier. The typical absorbance-time profile of Ni in presence of Li and Na matrix when ascorbic acid is used as chemical modifier is shown in Fig. 3. As can be seen the suppressing effect of the pre-pyrolysed ascorbic acid on the appearance of the non-atomic spectral band attributed to the Li/Na matrix is observed. The Ni analytical signal is no affected in time, but the shape is modified being more sensitive. The organic acid when pre-pyrolysed by the graphite during pyrolysis could produce a renewed carbon thin layer, which suppresses the intercalation of Li/Na matrix on the wall of the graphite tube. It is worth to note that the use of larger ascorbic acid mass did not cause a further beneficial effect.

3.3. Analytical figures of merit

Five-point calibration curves have been constructed for Ni using both aqueous and matrix-matched standard solutions. The slopes of the two curves are compared by means of the *t*-test [10] and any statistically significant difference is found, indicating that the matrix interference in the measurement of Ni is overcome. The calibration curves are linear up to 35 μg L^{-1} with correlation coefficients better than 0.999 and the intercepts did not significantly deviate from zero. In Table 2 are reported the characteristic parameters of the calibration curves along with their standard deviations. The detection limit, based on three times the standard deviation of seven measurements of the blank sample solution to the slope of the calibration graph, are similar to those in aqueous

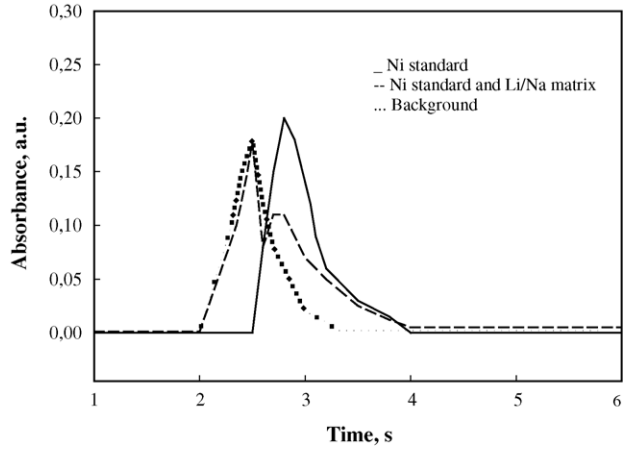

Fig. 2. Atomisation signals of 0.4 ng Ni both in aqueous (—) and 0.25 mol L^{-1} Li and 0.16 mol L^{-1} Na matrix (- - -) along with background absorption (....) in absence of chemical modifier.

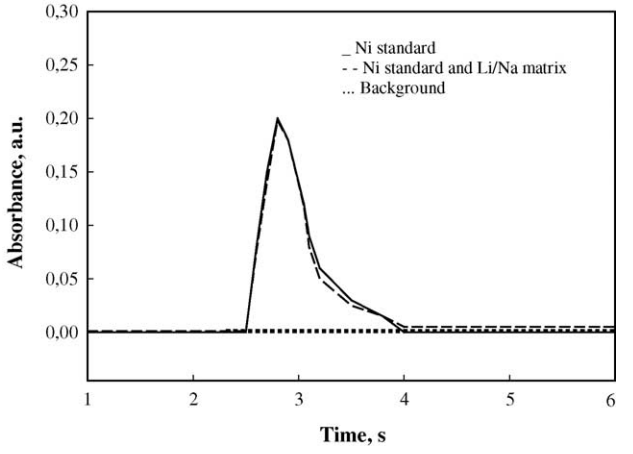

Fig. 3. Atomisation signals of 0.4 ng Ni both in aqueous (—) and 0.25 mol L^{-1} Li and 0.16 mol L^{-1} Na matrix (- - -) along with background absorption (....) in presence of chemical modifier.

Table 2
Characteristic parameters of the analytical calibration curves for the determination of Ni obtained by GF AAS

	Aqueous matrix	Li/Na matrix
Correlation coefficient, r^2 ($n = 5$)	0.9997	0.9991
Equation of the regression line (Abs vs. concentration, $\mu g\,L^{-1}$)	$y = 0.01045x + 1 \times 10^{-5}$	$y = 0.01050x + 7 \times 10^{-5}$
Centroid of the regression line (x, y)	15, 0.156	15, 0.158
Standard deviation of the slope, s_b	4×10^{-5}	5×10^{-5}
Standard deviation of the intercept, s_a	5×10^{-5}	9×10^{-5}
Working linear range ($\mu g\,L^{-1}$)	5–35	5–35

solutions, i.e. $1\,\mu g\,L^{-1}$, and is converted in solid detection limit, i.e. 5×10^{-8} g Ni per gram of melt by multiplying the calculated value by the dilution factor. The reliability of the proposed method is assessed by analysing a series of synthetic samples because certified values of Ni in Li_2CO_3 and Na_2CO_3 are not available. The synthetic samples are prepared by adding known amounts of Ni to Li/Na carbonate solutions so that the final matrix in analysis is simulated. The percentage recoveries ranged from 99 to 101% and are in good agreement with those obtained using the method of standard additions. The precision, expressed as relative standard deviation, is better than 3% ($n = 5$) at the $20\,\mu g\,L^{-1}$ level. Approximately 250 firings have been carried out using ascorbic acid as chemical modifier without any appreciable loss of Ni sensitivity.

3.4. Analysis of melts

The results of the analysis of nickel in $(Li_{0.52}Na_{0.48})_2CO_3$ melt samples withdrawn at different times are shown in Table 3. The amount of nickel increases with the increasing of the time up to 144 h, after that the value of nickel does not vary for more than 5%. As defined in reference [2] this value can be taken as the solubility value of nickel in Li/Na carbonate melt.

Table 3
Determination of Ni in real melt samples

Time (h)	Ni/$(Li_{0.52}Na_{0.48})_2CO_3$ ($\times 10^{-6}$ g/g)[a]	$X_{Ni} \times 10^6 = n_{Ni}/n_{(Li_{0.52}Na_{0.48})_2CO_3}$ [b]
0	≤0.08	≤0.1
24	1.1 ± 0.1	1.8
48	2.3 ± 0.1	3.5
72	4.2 ± 0.3	6.5
96	4.4 ± 0.2	6.7
120	4.7 ± 0.2	7.2
144	4.5 ± 0.2	6.9
168	4.9 ± 0.2	7.4
192	4.6 ± 0.2	7.0
216	4.3 ± 0.2	6.5
240	4.5 ± 0.2	6.9
264	4.8 ± 0.2	7.3
288	4.8 ± 0.2	7.3

[a] Solid concentration ± standard deviation values obtained by multiplying each solution concentration value by the dilution factor.

[b] $X_{Ni} = n_{Ni}/n_{(Li_{0.52}Na_{0.48})_2CO_3}$ = mole fraction of Ni in the melt obtained by multiplying the solid concentration by the factor 1.52, i.e. 89.3 molecular weight of $(Li_{0.52}Na_{0.48})_2CO_3$/58.7 atomic weight of Ni; n_{Ni} = number of moles of nickel and $n_{(Li_{0.52}Na_{0.48})_2CO_3}$ = number of moles of lithium and sodium carbonates in the sample.

4. Conclusions

The proposed method allows the determination of trace levels of Ni in 52/48 mol.% Li_2CO_3/Na_2CO_3 melts by GF AAS using ascorbic acid as chemical modifier and calibration against acid-matched standard solutions. Moreover, the lifetime of the graphite tube is prolonged and the sensitivity for Ni is maintained over more than 250 firings.

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