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Short communication

Sensitive assay for oxygen solubility in molten alkali metal carbonates by indirect flame atomic absorption spectrometric Cr(VI) determination

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Abstract

A precise and accurate indirect analytical method for the assessment of O_2 solubility in molten $(Li_{0.62}K_{0.38})_2CO_3$ and $(Li_{0.52}Na_{0.48})_2CO_3$ is described. The method is based on the oxidation of $Cr_2(SO_4)_3$ (added in excess to the melt) by the oxygenate species, which are formed inside the melt when it is in contact with oxygen gas, and subsequent determination of trace amount of Cr(VI) in withdrawn frozen melts by flame atomic absorption spectrometry (FAAS). The samples (1.0–2.0 g) are dissolved in dilute hydrochloric acid at room temperature. The speciation of Cr(VI) is carried out by complexation with ammonium pyrrolidine dithiocarbamate (APDC), followed by extraction into methyl isobutyl ketone (MIBK), which is introduced directly into the flame. Optimisation of the flame composition provided maximum Cr signal in organic phase under lean acetylene-air flame. The separation and preconcentration parameters such as sample volume/extractant volume ratio, pH sample solution, chelating concentration and extraction time are evaluated. Under the optimised conditions Cr(VI) is efficiently separated from Cr(III), which exceeded 200-folds. The results of the analysis of synthetic samples using standards in MIBK medium give rise to recoveries of 98–99%. The Cr(VI) detection limit of 4×10^{-6} g L^{-1} using 12.5-fold preconcentration and relative standard deviation of 1% at the 0.10 mg L^{-1} level are obtained. The sampling-to-sampling reproducibility was typically 3–5% relative standard deviation. By changing the preconcentration factor and the dilution of the sample melt, it is possible to analyse oxygen concentrations in molten alkali metal carbonates as low as 1.5×10^{-9} mol O_2 per gram melt.

Keywords: Oxygenate species; Cr speciation; Flame atomic absorption spectrometry; Molten carbonates

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1. Introduction

The knowledge of oxygen solubility in $(Li_{0.62}K_{0.38})_2CO_3$ and $(Li_{0.52}Na_{0.48})_2CO_3$ eutectic melts is of great interest in the technology of molten carbonate fuel cells (MCFCs), because the cathode performance mostly depends on this physico-chemical property. In fact, the oxidant gas (O_2) may dissolve into the electrolyte (molten carbonates) as molecular oxygen, peroxide or superoxide, which are then available for the cathodic reduction. In general, literature information on oxygen solubility in molten alkali carbonates is sparse and sometimes conflicting due to the experimental difficulties involved in such measurements. In the course of past years, a number of methods have been used for analysis of dissolved oxygen in molten carbonates. Several methods have been used for the analysis of dissolved oxygenate species in molten carbonates. A katharometer-based analysis of gases evolved from quenched samples of melt have been developed [1,2]. Others have used amperometric titration with Na_2SO_3 powder [3] or addition of an excess of $Cr_2(SO_4)_3$ powders and chromate determination by standard iodometric [4] or spectrophotometric analysis [5]. A common feature of all these measurements is that they are invariably plagued by large data uncertainties since the low solubility values of oxygen in the carbonate melts (of the order of some fraction of 10^{-6} mol O_2 per gram molten alkali metal carbonates at 650 °C) challenge the detection limits of the above mentioned analysis methods. It is worth mentioning that very recently a new more sensitive method has been proposed based on addition of excess uranium dioxide followed by titration of urinates [6], although the practicability of this method appears rather questionable considering

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the use of radioactive reagents. Therefore, there is a need of more sensitive analytical methods for the assessment of oxygen solubility in molten alkali metal carbonates.

In the present paper, we propose an indirect analytical method for the assessment of O_2 solubility in $(Li_{0.62}K_{0.38})_2CO_3$ and $(Li_{0.52}Na_{0.48})_2CO_3$ eutectic melts. This study has been realized by applying a variation of the redox titration method described in [4] that exploits the oxidation of Cr(III) ion (added in excess as $Cr_2(SO_4)_3$) to $CrO_4{}^{2-}$ by the oxygen species dissolved into the electrolyte. The precision of our method derives from the fact that the trace amounts of Cr(VI) in withdrawn frozen melts are being detected by a highly sensitive instrumental technique such as the flame atomic absorption spectrometry after application of an extraction/preconcentration step.

The speciation of the hexavalent chromium is carried out by the well-known ammonium pyrrolidine dithiocarbamate (APDC) complexation/methyl isobutyl ketone (MIBK) extraction technique [7]. This technique allows in fact to separate the analyte from the interfering matrix constituents and to preconcentrate it in order to bring its concentration to a level suitable for the instrumental response. Although it is an easy to use and economic technique, the separation of trace level of Cr(VI) from large amount of Cr(III) has been not addressed sufficiently in the literature. Among the atomic spectroscopy to be coupled to liquid–liquid extraction technique [8], FAAS is less prone to matrix interferences, other than fast and low-cost, compared to other more sensitive spectroscopic instrumentation like graphite furnace atomic absorption spectrometry (GFAAS) [9] and inductively coupled plasma mass spectrometry (ICP-MS), where blockage of orifice nebuliser and difficulties in introducing organic solvent into the plasma limit its use [10,11]. This method allows to extend reliable oxygen solubility measurements even at low MCFC temperatures.

2. Experimental

2.1. Apparatus

A Varian 220FS flame atomic absorption spectrometer equipped with a deuterium lamp for background correction was used. A pneumatic nebuliser with a glass impact bead and an air-acetylene burner were used. Cr hollow cathode lamp was used. The most sensitive analytical wavelength at 357.9 nm was chosen for chromium measurements. Bandwidth was 0.2 nm. Integration time was 4 s. Observation height was varied between 6 and 12 mm. The flame composition was optimised as follows: the air flow rate was kept constant while the acetylene flow rate varied between 1.5 and 3.5 mL min^{-1}.

pH of the aqueous solutions was measured with a SA520 pH-meter (Orion, Beverly, MA, USA), using a C2005-8 red rod combined pH electrode (Radiometer, Copenhagen, Denmark). For calibration, standard buffer solutions from Aldrich were used. The pH of the sample solutions was varied up to 3.0 with 1 M NH_4OH.

2.2. Reagents and standard solutions

All acids and reagents were of analytical-reagent grade. Ultra-high purity water with a specific resistance of 18 MΩ cm obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA) and filtered through a 0.22 μm membrane filter was used throughout.

Ammonium pyrrolidine dithiocarbamate (APDC) from Merck was used for the preparation of 1–10% (m/v) solution by dissolving the appropriate amount in deionised water with stirring. The solutions were filtered, purified by extraction with methyl isobutyl ketone (MIBK, pro analysis Merck), and stored in a glass bottle. MIBK was saturated with deionised water and was confirmed to have negligible blank levels of chromium.

A stock standard Cr(VI) solution (1000 mg L^{-1}) was prepared by dissolving the appropriate amount of potassium dichromate (Merck) (previously dried at 150 °C) in deionised water. A stock standard Cr(III) solution (1000 mg L^{-1}) was prepared by dissolving the appropriate amount of $CrCl_3 \cdot 6H_2O$ in deionised water. Working standard Cr(VI) solutions were prepared daily in the range 0.10–2.5 mg L^{-1} by appropriate dilution of the stock standard solution with 1% (v/v) hydrochloric acid. These working standard solutions were extracted into MIBK after complexation with APDC and used for optimisation of the flame composition and height of observation above the burner. Working standard Cr(VI) solutions in the concentration range 0.01–0.20 mg L^{-1} were also prepared and submitted to the same separation/preconcentration procedure as for the sample solution. A multi-element standard solution of Cr(VI) and Cr(III) in the molar concentration ratio 1:200 was also prepared for the optimisation of separation process. Appropriate amounts of lithium, potassium, and sodium carbonate (Merck) were dissolved in water to make 0.50 M Li + 0.32 M K and 0.46 M Li + 0.42 M Na solutions, respectively, and used as the blank solutions for interfering studies. The impurities in the carbonate mixtures were all under the limit of detection of the proposed method.

2.3. Procedure

2.3.1. Solubility measurements

The measurements of O_2 solubility were carried out using the apparatus schematically depicted in Fig. 1. Commercial salts of alkali metal carbonates (Merck, PA) were previously dried at 300 °C for 24 h in air and mixed in a planetary mill for 24 h. Two eutectic mixture of alkali metal carbonates were used in this study, namely 62 mol% Li_2CO_3 + 38 mol% K_2CO_3 and 52 mol% Li_2CO_3 + 48 mol% Na_2CO_3, respectively. Fifteen grams of the mixtures were introduced in a 50 cm^3 alumina crucible, placed in an alumina cell inside a

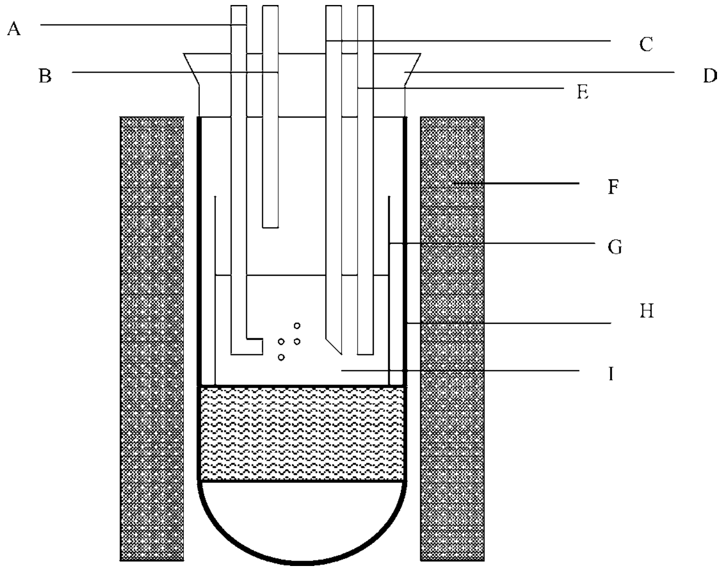

Fig. 1. Schematic drawing of apparatus for oxygen solubility measurements: A, gas inlet; B, gas outlet; C, sampling pipette; D, gas-tight flange; E, alumina tube sheathed thermo-coupled; F, furnace; G, alumina crucible; H, alumina cell and I, electrolyte.

furnace. The temperature inside the cell was raised to 400 °C under CO_2 at 100 ml min^{-1} flow rate for 24 h and then to 600, 650 and 700 °C under the same atmosphere. When the final temperature was reached the CO_2 gas was replaced with a gas mixture of O_2/CO_2 of known composition (20/80, 50/50 and 80/20% (v/v)), which was kept to bubbling into the melt for 3 h. Afterwards, the gas was stopped and a mixture of CO_2/Ar of the same CO_2 partial pressure of the gas composition was used as purge gas. Successively, about 70 mg of $Cr_2(SO_4)_3$ (previously dried and finely grounded) were carefully introduced through an alumina tube, previously immersed into the melt, as shown in Fig. 1. After equilibration for different times, approximately 1 g aliquots of the molten carbonates was sampled using a pure alumina pipette and sucked with a suction syringe (polypropylene syringe, Aldrich). The sampled yellowish melt was transferred to an aluminium pan where solidified. Then, an accurately weighed sample between 1.0 and 2.0 g of withdraw frozen melt was transferred to 25 mL covered beaker and dissolved in 2 mL of concentrated hydrochloric acid at room temperature. After complete dissolution, the solution was transferred to 25 mL clean volumetric flask and made up to volume with deionised water.

2.3.2. Cr(VI) separation/preconcentration procedure

A measured volume of sample solution (25 mL) was transferred to a volumetric flask (50 mL) and added 5 mL of 1–10% (m/v) APDC solutions to obtain a 0.2–2% (m/v) final concentration after dilution to 30 mL. The resulting solution was vigorously shaken by hand for 2 min and then 1–5 mL of MIBK were added and again vigorously shaken for different times (5–20 min). The organic phase was separated in a 40 mL Pyrex-glass separating funnel and aspirated directly into the flame of AAS.

3. Results and discussion

3.1. Optimisation of instrumental parameters

The organic solvent MIBK exhibits ideal combustion properties in the flame, sometimes showing enhanced sensitivity and nebulisation efficiency [12]. However, it has been observed that the efficiency of atomisation for chromium in MIBK medium is diminished under the flame conditions where the maximum absorbance value is observed for chromium in aqueous medium. In Fig. 2 is showed the influence of the flame composition on the absorbance signal of 2.5 mg L^{-1} Cr(VI) in both aqueous and organic medium at different high of observations above the burner head. The effect of acetylene flow rate and observation height seems to be more significant for chromium in MIBK than in aqueous solution. However, the maximum absorbance signal for Cr(VI) in MIBK is achieved with acetylene flow rate around 1.5 L min^{-1} and observation height of 8–12 mm. A non-specific absorbance signal (0.010 a.u.) of the organic phase is observed at the wavelength of chromium. The background level is very low and easily corrected by using deuterium background correction system, which does not affect the sensitivity.

3.2. Optimisation of the separation/preconcentration of Cr(VI)

It is well recognised that the separation of Cr(VI) from Cr(III) by complexation with APDC under certain conditions (concentration of chelating agent and pH solution) is based on their different affinity for the chelating agent. In fact, Cr(III) has a slow rate of reaction with APDC to form a stable complex because it forms strong aqua/hydroxo complexes

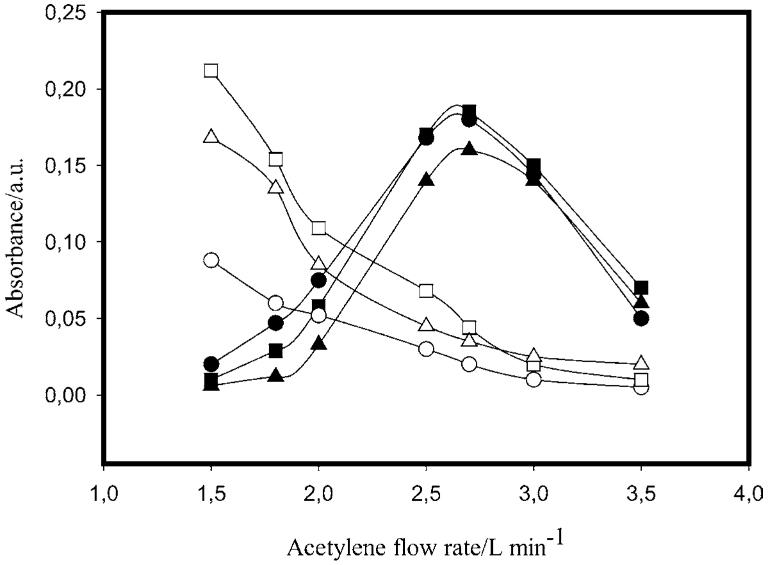

Fig. 2. The effect of acetylene flow rate on absorbance signal of 2.5 mg L^{-1} Cr both in aqueous (black symbols) and organic (MIBK) (white symbols) solutions at different observation heights: 6 mm (○); 8 mm (□) and 12 mm (△).

in aqueous solutions [13,14]. On the other hand, Cr(VI) is reduced by carbammate to Cr(III) and forms with APDC two type of complexes, denoted in literature as Cr(VI)–PDC, which are both extracted in MIBK. Therefore, optimisation of the extracting conditions like the acidity of the sample solution, the chelating agent concentration, the shaking time needed to establish the distribution of the complex Cr(VI)–PDC between the aqueous and organic phases and the sample volume/MIBK volume ratio is mandatory.

It is known that the pH of the sample solution on the aqueous-organic extraction process is very important because the formation of the metal complex mostly depends on the form of the complexing agent at a given pH. It has been reported that the complex Cr–APDC is stable over 1 month if the pH of the sample solution is kept between 1.8 and 3.0 [15]. The efficiency of extraction of Cr(VI) aqueous solutions containing Cr(III) 200-folds excess has been study as a function of the acidity of the aqueous phase. In Fig. 3 is showed the effect of aqueous solution pH on the efficiency of extraction process. As can be seen any remarkable effect of aqueous solution acidity up to pH = 3.0 has been noted on the extraction process. Therefore, the pH of the sample solution in the range 1–2 has been not changed in further study.

The complexation efficiency with APDC has been studied as a function of concentration of ligand reagent. In the range of concentration studied (0.2–2% (m/v)) a quantitative extraction efficiency has been observed being the recov-

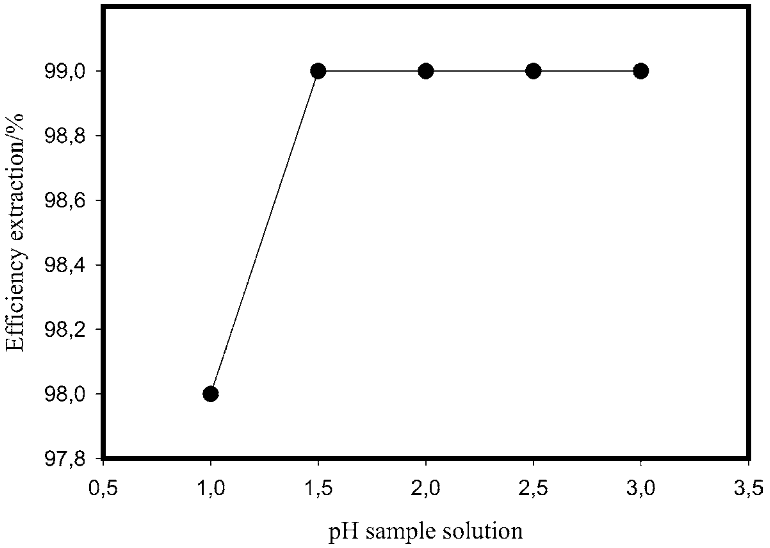

Fig. 3. The effect of acidity of 0.1 mg L^{-1} Cr(VI) sample solution on efficiency of extraction process.

Table 1
Recovery of preconcentrated Cr(VI) synthetic sample solution[a]

Volume of MIBK	Preconcentration factor[b]	Cr(VI) (10^{-6} g)		Recovery (%)
		Added	Found	
5.0	5.0	12.5	12.3	98
2.5	10.0	25.0	24.8	99
2.0	12.5	31.2	30.9	99

[a] Volume of synthetic sample solution 25 mL^{-1} and Cr(VI) concentration 0.10 mg L^{-1}.

[b] Calculated as volume of sample solution/volume of MIBK ratio.

Table 2
Recovery of Cr(VI) in synthetic sample solutions containing Cr(III) 200-folds excess

[a]Concentration of synthetic Cr(VI) solution (mg L^{-1})	Cr(VI) (10^{-6} g)		Recovery (%)
	[b]Added	Found	
0.002	0.625	0.612	98
0.010	3.12	3.10	99
0.020	6.25	6.18	99

[a] Volume of synthetic sample solution 25 mL^{-1}.

[b] Preconcentration factor 12.5.

ery between 99 and 100%, therefore a solution of 1% (m/v) APDC has been used thereafter.

The two-phase solutions have been shacked for different times and the separated organic phase introduced directly into the flame. It has been established that a time of 5 min is sufficient for a 100% extraction of Cr(VI)–PDC complex into MIBK. For shaken time of less than 5 min, the percentage of extraction was within 80–90%.

The preconcentration study has been carried out using a volume of 25 mL of 0.1 mg L^{-1} Cr(VI) standard solution and volumes of MIBK solution between 2 and 5 mL. The efficiency of the preconcentration process, expressed as percent recovery, has been evaluated by measuring the amount of Cr(VI) in the organic phase (extractant) and in the remaining aqueous phase (Table 1). It has been found that 2 mL of volume of organic phase has able for extracting quantitatively all Cr(VI) complex, thus that the maximum 12.5 preconcentration factor (calculated as ratio of volume of sample solution/volume of MIBK) may be reached.

The effect of an excess of Cr(III) on the extraction process of Cr(VI)–APDC complex has been also evaluated. Recovery test from synthetic samples spiked with Cr(III) and Cr(VI) in a molar up to 200:1 gives rise to quantitative extraction of Cr(VI) in the range 98–99% as shown in Table 2.

Table 3
Recovery of Cr(VI)[a] in synthetic sample solutions in presence of foreign elements

Foreign elements	Foreing elements concentration (mol L^{-1})	Recovery (%)
Li^+	0.50, 0.46	98
K^+	0.32	99
Na^+	0.42	99
Cl^-	1	99

[a] Cr(VI) concentration 0.10 mg L^{-1}.

Although APDC does not form complex with alkali metal like Li^+, K^+ and Na^+ as well with Cl^- anions their influence on the preconcentration process was evaluated by recovery test and the results reported in Table 3. As it can be seen any interference of foreign elements has been observed, being the Cr(VI) recovery within 99%.

3.3. *Analytical figures of merit*

Calibration graphs against seven standard solutions both in aqueous and in MIBK medium have been constructed in the range of concentration 0.10–2.5 mg L^{-1}. The figures of merit are tabulated in Table 4. The calibration curves are linear over the entire concentration range studied with correlation coefficient (r^2) better than 0.9999 and the intercepts does not significantly deviate from zero at 95% confidence level. The precision of the analytical method, expressed as relative standard deviation, is less than 1% at the 0.20 mg L^{-1} level. The sample-to-sample reproducibility, calculated by analysis of five samples, is within 3–5%, therefore the relative standard deviation of 4–6% is the cumulative error in the sampling and analytical measurements [16]. Method detection limit is calculated as three times the standard deviation of the mean of seven replicates of the reagent blank divided by the slope of the calibration graph obtained in both aqueous and MIBK medium. The Cr(VI) detection limit using 12.5-fold preconcentration has been found to be 0.004 mg L^{-1}.

Table 4
Characteristic parameters of the calibration curves against standard Cr(VI) solutions both in aqueous and MIBK medium obtained by FAAS

	MIBK	Aqueous
Correlation coefficient, r^2 ($n = 7$)	0.99998	0.99997
Equation of the regression lines (abs vs. concentration (mg L^{-1}))	$y = 0.08887x + 9 \times 10^{-4}$	$y = 0.07577x + 5 \times 10^{-4}$
s_b = standard deviation of the slope	5×10^{-5}	4×10^{-5}
s_a = standard deviation of the intercept	3×10^{-4}	5×10^{-4}
Working linear range (mg L^{-1})	0.10–2.5	0.10–2.5
Detection limit (3s) (mg L^{-1})	0.05	0.05
Detection limit (3s) using 12.5-fold preconcentration (mg L^{-1})	0.004	–

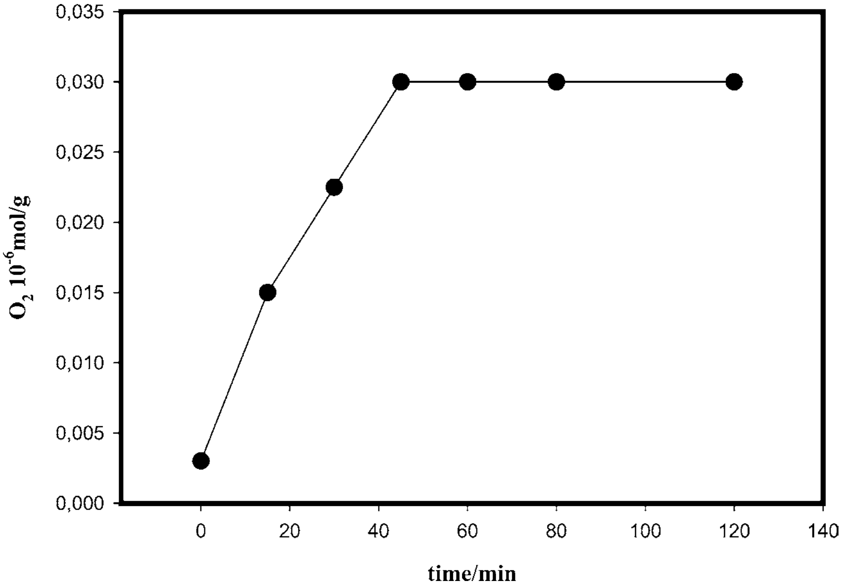

Fig. 4. Time dependence of O_2 solubility in $(Li_{0.52}Na_{0.48})_2CO_3$ eutectic melt at 650 °C and 20/80 (v/v) O_2/CO_2.

3.4. Analysis of melts

The establishment of the equilibrium conditions are very important for determining the solubility value. The oxygenate species that are postulated to be formed inside the melt when it is in contact with oxygen gas are: molecular oxygen, peroxide and superoxide ions. According to Broers et al. [4] the quantitative reaction of Cr(III) takes place with all forms of dissolved oxygen. For sake of simplicity, in the following equilibrium only reaction with the molecular oxygen is considered:

$$\frac{3}{4}O_2 + Cr^{3+} + \frac{5}{2}CO_3{}^{2-} \leftrightarrow CrO_4{}^{2-} + \frac{5}{2}CO_2 \qquad (1)$$

After addition of an excess of Cr(III) the oxygenates come in contact with it by chemical diffusion and consequently formation of Cr(VI). Therefore, the time needed to bring the Cr(VI) concentration to a constant value has been found. It is worth to note that the Cr(III) is oxidised only by the oxygenates present into the melt as showed by a parallel run using Ar as gas atmosphere. Any trace of Cr(VI) has been detected when an inert gas surrounds the melt. Fig. 4 shows the dependence of oxygen content dissolved in the eutectic Li–Na carbonate (previously saturated with 20/80 (v/v) O_2/CO_2 at 650 °C) as a function of time. The concentration of oxygen has been calculated on the basis of the Cr(VI) FAAS determination and taking into account the reaction (1). The equilibrium solubility is defined as the value of oxygen concentration that does not vary more than 5% over the time. It can be immediately appreciated from Fig. 4 that the apparent O_2 concentration reaches a stationary value after 45 min.

The results of the determination of oxygen in the frozen $(Li_{0.62}K_{0.38})_2CO_3$ and $(Li_{0.52}Na_{0.48})_2CO_3$ eutectic melts sampled under different conditions (such as temperature and oxygen partial pressure) are reported in Tables 5 and 6, respectively. From these data it is seen that the oxygen content in the frozen sampled melt is a function of the oxygen partial pressure above the melt and temperature. In general, our results are consistent with those of earlier studies [1,4] showing a distinct tendency for oxygen to be more soluble in Li–K than in Li–Na carbonate melts. The gathered oxygen concentration varied within one order of magnitude. Therefore, by changing the dissolution of sample melt and the preconcentration factor is possible to analyse oxygen concentrations in molten alkali metal carbonates as low as 1.5×10^{-9} mol O_2 per gram molten alkali metal carbonates.

Table 5
Results of oxygen concentration (10^{-6} mol g^{-1}) in Li–K carbonates at different temperatures and oxygen partial pressures

	600 °C	650 °C	700 °C
O_2/CO_2 (v/v)			
80/20	0.070 ± 0.003	0.160 ± 0.005	0.200 ± 0.010
50/50	0.040 ± 0.002	0.080 ± 0.004	0.110 ± 0.005
20/80	0.025 ± 0.001	0.035 ± 0.001	0.050 ± 0.002

Mean ± standard deviation of five melt samples.

Table 6
Results of oxygen concentration (10^{-6} mol g^{-1}) in Li–Na carbonates at different temperatures and oxygen partial pressures

	600 °C	650 °C	700 °C
O_2/CO_2 (v/v)			
80/20	0.051 ± 0.002	0.125 ± 0.005	0.180 ± 0.005
50/50	0.045 ± 0.004	0.065 ± 0.003	0.075 ± 0.003
20/80	0.025 ± 0.001	0.030 ± 0.001	0.050 ± 0.002

Mean ± standard deviation of five melt samples.

4. Conclusions

The assessment of oxygen solubility in molten $(Li_{0.62}K_{0.38})_2CO_3$ and $(Li_{0.52}Na_{0.48})_2CO_3$ has been carried out by an indirect method, based on the separation of Cr(VI) (formed in situ oxidation of Cr(III) by the oxygenate species present into the melt) as APDC complex and successively preconcentrated/extracted in MIBK and analysed by FAAS. The method is simple and fast allowing to determine accurately and precisely oxygen concentration in molten alkali metal carbonates as low as 1.5×10^{-9} mol O_2 per gram molten alkali metal carbonates. The proposed methodology may be also applied to the determination of oxygen solubility in molten alkali metal salts.

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