Article

Determination of Some Inorganic Species of Fe, Mn and Cr by Chemical Vapor Generation Hyphenated with Inductively Coupled Plasma Atomic Emission Spectrometry

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Este trabalho descreve a geração de espécies voláteis (CVG) dos íons Fe^{2+}, Fe^{3+}, Cr^{3+}, CrO_4^{2-}, Mn^{2+} e MnO_4^- pela reação com o agente redutor $NaBH_4$ em HCl, CH_3COOH e ácido cítrico usando um sistema de separação gás-líquido e espectrometria de emissão óptica em plasma com acoplamento indutivo (ICP OES). As condições otimizadas foram obtidas usando baixas concentrações de HCl (0,05-0,075 mol L^{-1}) e $NaBH_4$ (0,25-1,0% (m/v)). As espécies voláteis foram geradas de forma mais eficaz para o estado de oxidação mais baixo dos íons estudados. Limites de detecção de 10, 25 e 66 ng mL^{-1} foram obtidos para Mn^{2+}, Fe^{2+} e Cr^{3+}, respectivamente.

Generation of volatile species (CVG) from Fe^{2+}, Fe^{3+}, Cr^{3+}, CrO_4^{2-}, Mn^{2+} and MnO_4^- ions by reaction with $NaBH_4$ reductant in HCl, CH_3COOH and citric acids using gas-liquid phase separation system and inductively coupled plasma atomic emission spectrometry detection (ICP OES) was reported. The optimized conditions were obtained using low concentrations of HCl (0.05-0.075 mol L^{-1}) and $NaBH_4$ (0.25-1.0% (m/v)). Volatile species were more effectively generated for lower oxidation state of the analytes. Detection limits of 10, 25 and 66 ng mL^{-1} were achieved for Mn^{2+}, Fe^{2+} and Cr^{3+}, respectively.

Keywords: chemical vapor generation, transition metals, speciation forms, inductively coupled plasma optical emission spectrometry

Introduction

In atomic spectrometry, chemical vapor generation (CVG) is a well known sample introduction technique used for determination of hydride-forming elements (*e.g.* As, Bi, Sb) at trace level.[1] Recently, the list of the elements reduced to volatile species with sodium tetrahydroborate, $NaBH_4$ (THB), in acidic medium, has been meaningfully extended. In the group of transition and noble metals, generation of volatile compounds of Cd,[2-5] Cu,[3,4,6,7] Ni,[3,4,6,8] Zn,[2-4,9] Ag,[3-6] Au,[3,5-7,10] Pd,[6,7,10] or Rh[6,7] has often been reported. In light of former research work, experimental parameters including reductant-acid combination (especially the type of acid and its concentration[2-10] and THB concentration[3,5-9]) were found to influence the efficiency of the CVG processes. However, chemical vapor generation of transition and noble metals is far from being "mature", mainly due to the instability of the volatile species.

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Concise review devoted to transition metal was presented lately by Matoušek.[11] Reports which focus on applying CVG processes to produce volatile species of Fe, Mn and Cr are scarce. Wickstrøm *et al.*[12] were the first who considered transport of the Fe^{3+} and Cr^{3+} ions into plasma at THB-HCl condition. They showed that it is due to transport of the fine aerosol. Pohl and Zyrnicki[13] reported enhanced sample introduction efficiencies for Fe and Cr in the reaction with THB and HNO_3, whereas transport of Mn was realized only by an aerosol formation. Similarly, Peña-Vázquez and co-workers,[3] during their interference study on Ag, Au, Cd, Cu and Ni vapor generation at the one optimized condition (HNO_3 + THB + 8-hydroxyquinoline), obtained volatile species of Fe and Cr. Dos Santos *et al.*[14] investigated a novel approach to the generation of Hg vapor and additionally tested applicability of this procedure to vapor generation of other metals (including Cr, Fe, Mn). Feng *et al.*[6] were the only ones who mentioned the existence of volatile Mn species generated from Mn^{2+} in the reaction of HNO_3 with THB.

Considering a lack of information on study of speciation forms (appearing in various oxidation states) of transition metals by the CVG application, the studies of the reactions of the ions of Fe (Fe^{2+}, Fe^{3+}), Mn (Mn^{2+}, MnO_4^-) and Cr (Cr^{3+}, CrO_4^{2-}) with THB in different acidic media were undertaken here by means of a CVG ICP OES (chemical vapor generation and inductively coupled plasma atomic emission spectroscopy, as detection method) hyphenated system. The influence of experimental conditions on analytical performance was investigated. Some analytical figures of merit as detection limit, linearity range and precision were evaluated.

Experimental

Chemical vapor generation

Vapors were generated in a continuous flow system with a gas-liquid phase separation. A scheme illustrating the system of chemical vapor generation coupled to the ICP OES spectrometer is shown in Figure 1.
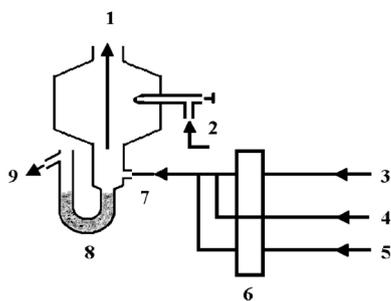

Figure 1. Scheme of chemical vapor generation system: (1) to the ICP OES, (2) Meinhard nebulizer (Ar carrier gas flow of 0.3 L min⁻¹), (3) sample (flow rate of 1 mL min⁻¹), (4) acid (flow rate of 1 mL min⁻¹), (5) reductant (flow rate of 1 mL min⁻¹), (6) peristaltic pump, (7) reaction coil, (8) phase separator (modified cyclonic spray chamber) and (9) drain.

The system consisted of a modified cyclonic spray chamber, a concentric pneumatic Meinhard nebulizer and peristaltic pumps with delivery tubes. The chamber was directly connected with a plasma torch. Sample and acid were simultaneously pumped in two separate streams to the first Y-junction and then were mixed with reductant solution in the second Y-junction. Then, through a 60 mm long tube (0.5 mm i.d.) the reaction mixture was introduced at the bottom of the chamber. Volatile species and other gaseous coproducts were swept by a carrier Ar stream, introduced through the nebulizer gas inlet, and transported into the plasma. The sample inlet of the nebulizer was clogged. The wastes were drained with the aid of a peristaltic pump. To achieve stability, the level of the post-reaction liquid in the chamber was controlled and kept at a constant level. The

same chamber and nebulizer were also used to nebulize the sample solution.

Apparatus

Measurements were performed using the Jobin Yvon sequential inductively coupled plasma emission spectrometer (JY 38S). Working parameters for CVG and ICP OES detection are listed in Table 1. After the reaction mixture passed into the chamber, 2 min were necessary to achieve steady signals of the analyzed species.

Table 1. The CVG ICP OES operating parameters

Generator / MHz	40.68
Rf power / W	1000
Injector i.d. / mm	2.5
Observation zone	12 mm above load coil
Ar flow rates / (L min⁻¹)	plasma gas: 13 sheath gas: 0.2 carrier gas: 0.3
Solution uptake / (mL min⁻¹)	sample: 1.0 acid: 1.0 reductant: 1.0
Replicates	3
Wavelength / nm: Feᵇ 259.9, Mnᵇ 259.4, Crᵇ 267.7, Bᵃ 249.7, Mgᵇ 280.3	

ᵃAtomic line; ᵇionic line.

Reagents and chemicals

All chemicals used were of analytical grade. The 1000 μg mL⁻¹ solutions of Fe^{2+}, Fe^{3+}, Mn^{2+}, MnO_4^-, Cr^{3+} and CrO_4^{2-} were prepared from their salts (POCh, Gliwice, Poland). Working standard solutions (up to 100 μg mL⁻¹ for calibration curves and 5 μg mL⁻¹ for other investigations) were obtained by dilution of the single-element standards. Solutions of hydrochloric and acetic acids were prepared from concentrated HCl, CH_3COOH (Merck, Darmstadt, Germany) and citric acid from solid $C_6H_8O_7 \cdot H_2O$ (POCh) reagent. The reductant solutions were made daily by dissolving THB powder (POCh) in 0.1 mol L⁻¹ NaOH (POCh). Solutions were filtered before being used. Deionized water (18.3 MΩ cm) was used in all experiments.

Results and Discussion

The line intensities were expressed here as net intensities (total signal intensity minus background intensity). The mean values were obtained from three repeated measurements with the relative standard

deviations (RSDs) ranged from 2 to 15%, depending on the experimental conditions.

Reaction of Fe, Mn and Cr ions with THB in HCl medium

The reactions of THB with the ions: Fe^{2+} and Fe^{3+}, Mn^{2+} and MnO_4^-, Cr^{3+} and CrO_4^{2-} in HCl, were studied. It was found that, Fe, Mn and Cr analyte signals were observed only at low concentrations of HCl (< 0.1 mol L^{-1}). It was also found that, Fe, Mn and Cr analyte signals depended on the HCl acidity and oxidation state of the elements (Figure 2). The signals from Fe^{2+}, Mn^{2+} and Cr^{3+} were 2-4 times higher than those achieved from Fe^{3+}, MnO_4^- and CrO_4^{2-}. Such behaviour is similar to that observed for hydride-forming elements (*e.g.* As, Sb, Se). The reasons for the higher signal for lower oxidation state of transition elements are complex and likely attributed mainly to changes in the kinetics of the reaction of ions with THB.
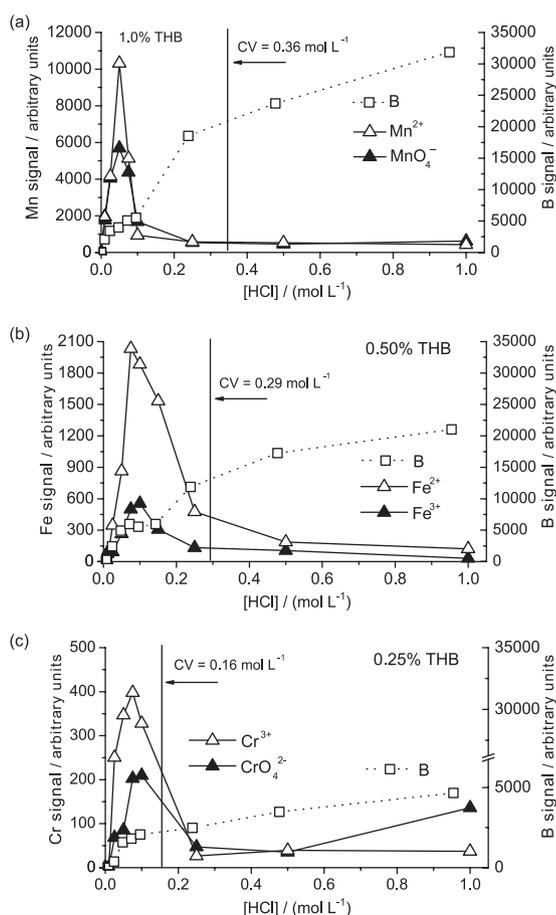

Figure 2. Responses of Mn (a), Fe (b) and Cr (c) species under chemical vapor generation condition.

To demonstrate that Fe, Mn and Cr are transported to ICP as volatile species, and not as a fine aerosol formed in the chamber due to a turbulent reaction between THB and acid, the sample solutions were spiked with 10 μg mL^{-1} of Mg. Magnesium is considered to be an element which does not form any volatile compounds with THB and is only transported in aerosol form. According to our previous work,[15] boron is transported to plasma in the same way. Behavior of the B and Mg signals on one side and the Fe, Mn and Cr signals on the other side was quite different. For clarity, only the analyte and boron lines were shown in Figure 2. The generation of Fe, Mn and Cr species took place only at low acidity, where reaction between the reductant and acid runs less violently. At higher turbulence, the Mg and B lines were more intensive, but analyte line intensities decreased drastically. Additionally, the CVG reactions with Fe^{2+} and Mn^{2+} ions were conducted in the presence of EDTA (a strong complexing agent). Suppression of the analyte responses was also observed. These results are clear evidence that Fe, Mn and Cr signals arise due to a chemical process. Transport of aerosol introduced with the gas phase into plasma during the CVG reaction was very small and depended on experimental conditions. For magnesium, it was measured to be about 0.005% in the range of volatile species generation, and at high turbulence of CVG reactions (1% (m/v) THB with 1 mol L^{-1} HCl) it did not exceed 0.01%.

Conditions for the generation of Mn, Fe and Cr vapors differed significantly from those for hydride-forming elements. The highest responses (Figure 2) were obtained much before the so called CV point (*critical value*), corresponded to the point at which the equivalent of acid is equal to the sum of THB + NaOH. Our results for Fe, Mn and Cr are in agreement with those reported as mild conditions for CVG, in the case of the transition metals.[6-9]

Effect of THB concentration in HCl medium

Vapor generation from Fe, Mn and Cr ions, with 0.25-3.0% (m/v) THB and 0.01-1.0 mol L^{-1} HCl, was examined. The results are given in Figure 3.

The dependencies of the Mn, Fe and Cr signals on the THB concentration were characteristic for each metal and were also similar among metal forms. Reaction runs more effectively for the lower oxidation states of the metals. The maximum signals of the Fe, Mn and Cr were found at different THB concentrations, but at similar HCl concentrations, *i.e.* 0.05-0.075 mol L^{-1}.

The Fe signal (Figure 3a) increased up to 0.5% (m/v) THB. Above this concentration the Fe emission decreased. For Fe^{2+} changes were significant and rapid. Reduction of Fe^{3+} was less efficient. In the region of 1-2% (m/v) THB, the Fe^{2+} signal was about 3 times higher than that from Fe^{3+}.

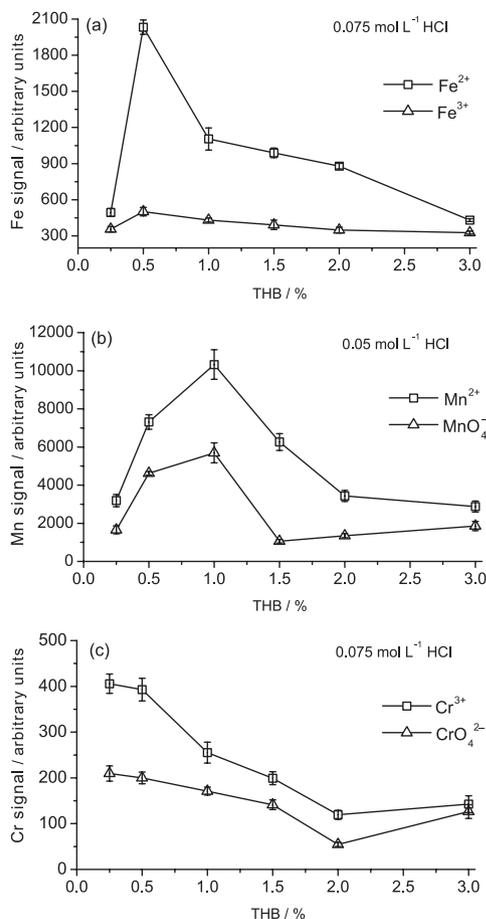The Mn signal from Mn ions (Figure 3b) increased with

Figure 3. Effect of the THB concentration on intensities of Fe (a) Mn (b) and Cr (c) species under chemical vapor generation condition.

the THB concentration. The highest Mn line intensity was obtained at 1.0% (m/v). Further growth in THB amounts caused a continuous decrease in the Mn signal for Mn^{2+}, and a rapid for MnO_4^-. The response obtained from MnO_4^- was, on average, *ca.* 2.5 times lower than the response from Mn^{2+}.

The relationships for Cr were quite different (Figure 3c). It was found that Cr volatile species could be effectively generated only at a very low THB concentration. The highest responses from Cr^{3+} and CrO_4^{2-} were attained at a THB concentration of 0.25% (m/v). For the higher THB amounts, the Cr signal was systematically reduced. The Cr^{3+} signal was around 2 times higher than that of the CrO_4^{2-} signal.

Summarizing, the 0.5, 1.0 and 0.25% (m/v) THB concentrations were observed here, as optimal for generation of the volatile Fe, Mn and Cr species, respectively.

Investigation of the HCl-THB effect on chemical vapor generation efficiencies of Fe, Mn and Cr species indicates that both HCl and THB are critical variables. As it was shown in Figures 2-3 the optimized conditions are different for all the elements investigated here. Generally, at selected and fixed HCl concentration we initially observed appearing

of distinct signal maximum increasing with concentration of THB. With further growth in THB concentration, signal maximum disappeared and the relation between analyte responce and HCl concentration was typical for aerosol transport to plasma.

Effect of acid type and concentration

The effect of the HCl, CH_3COOH and citric acid on the analytes responses was studied in a concentration range of 0.01 to 1.0 mol L^{-1}. An optimal THB concentration for Fe, Mn and Cr species generation were used. The results showing the highest reactivities for lower oxidation states of the metals were collected and compared in Figure 4.
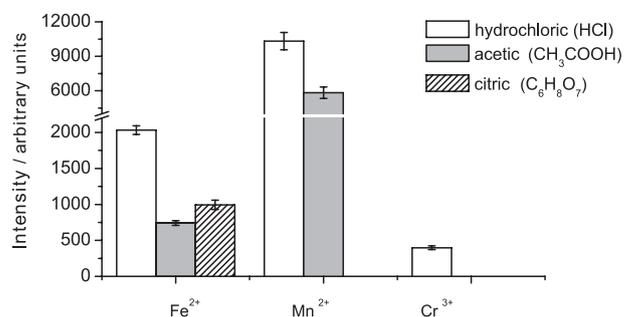

Figure 4. Effects of HCl, CH_3COOH and citric acids on signals from Fe^{2+}, Mn^{2+} and Cr^{3+} ions at optimized THB concentrations.

HCl was found to be the most favourable medium. At a concentration of 0.075 mol L^{-1} for Fe^{2+} and Cr^{3+}, and at a concentration of 0.05 mol L^{-1} for Mn^{2+}, the highest intensities of Fe, Mn and Cr lines were reached. At such conditions, the responses from Fe^{3+}, MnO_4^- and CrO_4^{2-} were 4.2, 1.8 and 2.2 lower than those of Fe^{2+}, Mn^{2+} and Cr^{3+}.

For CH_3COOH, the highest responses from Fe^{2+} and Mn^{2+} were obtained at a concentration of 0.075 mol L^{-1}, but their signals were 2-3 times lower than those obtained in HCl. In citric acid, the maximum of the Fe signal was shifted towards lower acidity. The maximum was reached at a concentration of 0.025 mol L^{-1}. In such a citric acid concentration, the Fe^{2+} response was 2 times lower in comparison to the signal obtained in 0.075 mol L^{-1} HCl. The Mn signal in citric acid, as well as the Cr signals in acetic and citric acids, were not sufficiently intensive to be measured.

Summarizing, HCl acid was found to be the best reaction medium for Fe, Mn and Cr volatile species generation.

Effect of the sample, acid and THB flow rates

The influence of the flow rates, of the reagents (i.e. sample, acid and reductant) on the analyte signals during

vapor generation from the Fe^{2+} Mn^{2+} and Cr^{3+} ions, was examined. It was found, that an increase in the flow rates from 0.25 to 1.0 ml L^{-1} led to a 6-fold enhancement of the signals. Above this point, the signals started to decrease and the repeatability of the measurements became poorer. Such an effect was probably due to a larger production of H_2, leading to instability of plasma. As a result, the reagent flow rates of 1.0 ml L^{-1} were used here.

Effect of the reaction coil length

Maximum Fe^{2+}, Mn^{2+} and Cr^{3+} responses were observed if the reaction coil was short. In our case it was a 6 cm coil. An increase in the coil length of up to 60 cm caused a 5-fold decrease in analyte signals.

Analytical performance

Under optimized CVG conditions, the analytical figures of merit for Fe, Mn and Cr species, *i.e.* the limits of detection (LOD), linear dynamic ranges (LDR), linearity coefficients (r^2), slopes of calibrations (a) and precision of measurements of analytes signal (expressed by RSD) were examined. The LOD, RSD and r^2 values as well as the slope coefficients are listed in Table 2. Table 2 includes also some results achieved for pneumatic nebulization (PN). Calibration graphs for Fe^{2+}, Mn^{2+} and Cr^{3+} were shown in Figure 5.

Table 2. Analytical performance using pneumatic nebulization and chemical vapor generation in optimized conditions for Fe, Mn and Cr species detection

λ / nm		LOD^a / (ng mL^{-1})	RSD / % (for 5.0 μg mL^{-1})	Slope	r^2
Fe 259.9	PN	2.6	2.8	36580	0.9973
	CVG	25 (Fe^{2+})	2.9	4327	0.9780
		84 (Fe^{3+})	3.2		
Mn 259.4	PN	0.98	1.6	80818	0.9973
	CVG	10 (Mn^{2+})	7.3	10652	0.9926
		18 (MnO_4^-)	8.5		
Cr 267.7	PN	4.1	3.4	13856	0.9967
	CVG	66 (Cr^{3+})	5.6	1567	0.9996
		174 (CrO_4^{2-})	8.6		

^{a}3σ criterion; n = 3.

Linearity of the Mn^{2+} and Cr^{3+} signals was observed to 100 μg mL^{-1}, although in the case of chromium two linear ranges could be distinguished. The Fe^{2+} signal was linear only up to 5 μg mL^{-1}. After that, the Fe^{2+} response was not proportional, and appearance of a black precipitate in the reacting mixture occurred.
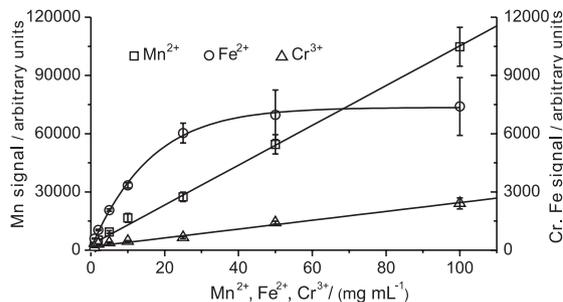

Figure 5. Calibration graphs for Fe^{2+}, Mn^{2+} and Cr^{3+} ions at the application of vapor generation.

The RSD values, noticed at chemical vapor generation from Mn^{2+} and Cr^{3+}, were higher than those observed when applying pneumatic nebulization for measuring Mn and Cr by ICP OES. Precisions of the ICP OES measurements of Fe using the CVG and PN technique were similar. For the CVG process the RSD values were dependent on the analyte concentration.

The LODs were about 2-3 times lower, on average, for the Fe^{2+} Mn^{2+} and Cr^{3+} than those for Fe^{3+}, MnO_4^- and CrO_4^{2-} The obtained values were about one order higher than those for PN. Efficiency of chemical vapor generation was calculated by comparison of CVG slopes with PN slopes. At a 2% efficiency of nebulizer-cyclonic chamber system used here, the following efficiency values were obtained: 0.26% for Mn^{2+}, 0.24% for Fe^{2+} and 0.23% for Cr^{3+}.

Our results for Fe and Cr are difficult to compare with those reported by Peña-Vázquez *et al.*[3] due to different experimental conditions applied in our investigation. Nevertheless, our LOD values were 3 times higher for Fe but 4 times lower for Cr.

Conclusions

For the first time, an investigation of chemical vapor generation of volatile species from Fe^{2+}, Fe^{3+}, Cr^{3+}, CrO_4^{2-}, Mn^{2+} and MnO_4^- ions in the reaction with THB in acidic media was demonstrated. Efficiencies of the volatile species formation were higher for lower oxidation states of metals. The optimal CVG conditions were far from typical conditions for hydride-forming elements in the borohydride generation technique. The influence of the experimental parameters on the response of the Fe, Cr and Mn analytes was very significant and stronger than in the case of such elements as *e.g.* As, Bi or Sb. The high effectiveness of the CVG process was observed for relatively narrow ranges of HCl (from 0.05 to 0.075 mol L^{-1}) and THB (0.5-1.0% (m/v)) concentrations. Results of analytical performance show that further studies devoted to improvement of the detection limits are necessary.

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