

## Determination of Trace Elements in Manganese Salts after Preliminary Matrix Separation

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### Abstract

The analytical procedure for trace elements (Co, Cr, Cu, Fe, Pb and Zn) determination in various manganese salts (manganese sulfate, manganese chloride) is described. Preliminary separation of matrix element is based on the different kinetics of reextraction of dithiocarbamate complexes of the trace elements and manganese. Analytical procedure consists of following steps: simultaneous extraction of dithiocarbamate complexes of analytes and matrix element in isobutylmethyl ketone (IBMK), reextraction of manganese dithiocarbamate in aqueous phase and FAAS or ETAAS measurement of trace elements in the organic phase. The method is adapted also for ICP-AES measurements by using the second step of reextraction of the trace analytes (after manganese reextraction) in 4 mol L<sup>-1</sup> HNO<sub>3</sub>. Several parameters which are the most important for quantitative separation of matrix element without losses of trace elements were optimized by using model experiments. Optimal instrumental parameters for ETAAS/FAAS measurements in IBMK are presented. The accuracy and precision of the proposed analytical procedure was verified by the method of standard additions and by comparative analysis using routine ETAAS after sample dissolution in H<sub>2</sub>O. Detection limits achieved are 0.01 µg g<sup>-1</sup> for Co, Cr, Cu (ETAAS determination) and Zn (FAAS determination) and 0.02 µg g<sup>-1</sup> for Fe (ETAAS determination) and Pb (ETAAS determination). Relative standard deviation varied in the range from 2 to 12% for all studied elements at levels of content from 0.04 to 1 µg g<sup>-1</sup>

**Keywords:** Microelements; Manganese salts; Liquid-liquid extraction; Atomic absorption spectrometry

### 1. Introduction

Manganese is an abundant element naturally occurring in minerals and is found in many types of rock. Manganese does not occur in the environment as a pure metal, but as a component of more than 100 minerals, including sulphides, oxides, carbonates, silicates, phosphates, and borates. The most significant application of manganese is in the production of

ferromanganese, or metallic manganese, which is used in the steel industry to improve hardness, stiffness, and strength of steel. Metallic manganese of relatively pure grade is the basic material for a series of alloys with special electrical and thermal characteristics. Impurities are generally in the range of ppm levels and less. The most important manganese compounds are manganese chloride ( $\text{MnCl}_2$ ); manganese sulphate ( $\text{MnSO}_4$ ); manganese tetraoxide ( $\text{Mn}_3\text{O}_4$ ); manganese dioxide ( $\text{MnO}_2$ ); and potassium permanganate ( $\text{KMnO}_4$ ). Pure manganese chloride is used as a precursor for other manganese compounds, as a catalyst in the chlorination of organic compounds, in animal food to supply essential trace minerals, and in dry-cell batteries. Pure manganese sulphate is used in glazes, varnishes, ceramics, and fertilizers; as a fungicide; and as a nutritional supplement. Therefore the determination of microimpurities in manganese compounds is important analytical task. The widely used method for such analysis is direct ETAAS which permits the determination of very low concentration of microelements with high accuracy. However matrix interferences from one side and the strong contamination of the graphite furnace with matrix element manganese restricted application of ETAAS in the analysis of high purity manganese salts. Therefore preliminary separation and preconcentration of trace elements is appropriate and useful approach in this case [1-3]. Various methods have been suggested as separation and preconcentration techniques such as: solvent extraction, column solid phase extraction, cloud point extraction, etc. [1-5]. Methods for the removal of manganese(II) from aqueous solutions are based mainly on coprecipitation of manganese(II) as the sulphide with iron(III) or lanthanum(III) or liquid/liquid extraction of dithiocarbamate, oxinate, or thiooxinate complexes using various anion-exchangers [6-10]. There are only few papers dealing with trace elements preconcentration from manganese salts. Selective separation and determination of Au, Ag and Pd has been achieved by sorption of their complexes with dithiophosphoric acid on activated carbon [11]. Preconcentration of Cu (II), Fe(III), Ni(II), Co(II) and Pb(II) in the presence of Mn-salts has been proposed by using solid phase extraction of their dithiocarbamate complexes on Chromosorb-102 resin [12]. Thorium (IV) and U(VI) have been determined in manganese nodules by sorption on anion-exchange resin Bio Rad AG-1, X-8 [13]. In this work, we proposed a method for separation and preconcentration of trace elements (Co, Cr, Cu, Fe, Pb and Zn) by simple and rapid liquid-liquid extraction into isobutylmethyl ketone. The separation of matrix element Mn from trace elements is based on different kinetics of reextraction of its dithiocarbamate complex. Chemical parameters e.g. the amount and type of extraction reagent, extraction time, reextraction time for  $\text{Mn}(\text{DTC})_2$  are optimized and defined. The validity of the analytical procedure developed is confirmed by added/found method and comparative analysis of manganese salts by ETAAS after sample dissolution in  $\text{H}_2\text{O}$ . The method is applied for the analysis of high purity Mn-salts.

## 2. Experimental

### 2.1. Instrumentation

A Thermo Model Solaar 2 flame atomic absorption spectrometer with air/acetylene flame was used for flame atomic absorption measurements. Instrumental parameters are optimized according to the Manual. A Varian SpectrAA 640 Z Zeeman electrothermal atomic absorption spectrometer with a Varian PSD-100 Autosampler was used. Hollow cathode lamps were used as light sources. Optimal instrumental parameters used for ETAAS measurement of Co, Cr, Cu and Pb in IBMK are given in Table 1.

### 2.2. Reagents and samples

All reagents and standards were of analytical reagent grade. Stock solutions of Co, Cr, Cu, Fe, Pb and Zn are delivered by Solution Plus Inc. (USA) with the concentration of 1 mg mL<sup>-1</sup>. Diluted working standard solutions were prepared weekly by appropriate dilution. Doubly distilled water was used throughout. High purity manganese salts were used for model investigations.

**Table 1.** Instrumental parameters for ETAAS determination of Co, Cr, Cu and Pb in IBMK

Element	Co	Cr	Cu	Fe	Pb
Wavelength/nm	242.5	357.9	327.4	248.3	283.3
Slit/nm	0.2	0.5	0.5	0.5	0.5
Lamp current/mA	7	7	4	5	5
Calibration mode	Absorption, peak area				
Background correction	Zeeman				
Drying					
Temperature/°C	95	95	95	95	95
Ramp time/s	40	40	40	40	40
Temperature/°C	120	120	120	120	120
Ramp time/s	10	10	10	10	10
Pretreatment					
Temperature/°C	750	1000	800	1000	400
Ramp time/s	5	5	5	5	5
Hold time/s	20	20	20	20	20
Atomization					
Temperature/°C	2300	2600	2300	2000	1900
Ramp time/s	1	1	1	1	1
Hold time/s	2	2	2	2	2
Cleaning					
Temperature/°C	2600	2600	2600	2600	2600
Hold time/s	2	2	2	2	2

### 2.3. Procedures

*Matrix separation:* Manganese salt sample ca. 0.3 g was placed in an extraction cylinder (30 mL) and dissolved in 20 mL doubly distilled water, 2 mL of acetate buffer were added in order to achieve pH=4.5 and then 0.5 mL aqueous solution of ammonium pyroliidinedithiocarbamate (APDC, 1%, *m/V*). Extraction was carried out with 10 mL (for model experiments) or 3 mL (for ETAAS measurements) isobutylmethyl ketone (IBMK) for 1 min. After 2.5 hours Mn(DTC)<sub>2</sub> was spontaneously reextracted into the inorganic phase.

*Procedure A,* ETAAS/FAAS determination of trace elements: Trace elements Co, Cr, Cu, Fe, Pb and Zn were determined directly in the organic phase without phase separation by atomic absorption spectrometry (FAAS or ETAAS).

*Procedure B,* ICP-AES determination of trace elements: Trace elements Co, Cr, Cu, Fe, Pb and Zn were measured by ICP-AES after reextraction in 3 mol L<sup>-1</sup> HNO<sub>3</sub>.

*Procedure C,* ICP-AES determination of trace elements: Extraction step for matrix separation was carried out with 10 mL diisopropyl ether (DIPE). After reextraction of Mn(DTC)<sub>2</sub> organic phase was evaporated till dryness and the residue was dissolved in 3 mol L<sup>-1</sup> HNO<sub>3</sub> for ICP-AES measurement of trace elements.

## 3. Results and discussion

### 3.1. Optimal conditions for matrix separation

The separation procedure optimized in the present study is based on different kinetics of reextraction of the dithiocarbamate complexes of the matrix element manganese and trace elements Co, Cr, Cu, Fe, Pb and Zn. It is well known that manganese as well as the trace elements formed stable dithiocarbamate complexes which can be extracted quantitatively in organic solvent. The optimal pH ranges for quantitative extraction of different elements are slightly different, however it is accepted that pH from 5 to 7 is a good compromise. However the kinetics of reextraction is quite different and the most unstable dithiocarbamate is Mn(DTC)<sub>2</sub>. [14, 15]. Several factors influencing the degree of separation of trace elements from matrix element Mn were optimized.

### 3.2. The type and amount of extraction reagent

Two extraction reagents were tested: hexamethylenammonium hexamethylenedithiocarbamate (HMA-HMDTC) and ammonium pyroliidinedithiocarbamate (APDC). Experiments performed showed that quantitative extraction for all studied trace elements in the

pH range 4 to 6 is ensured by APDC, the degree of extraction of Mn is  $64\pm 6\%$ . For HMA-HMDTC quantitative extraction of trace elements is achieved at higher pH values 7-8, with higher degree of extraction of matrix element Mn,  $90\pm 7\%$ . Therefore APDC was used as extraction reagent in the next optimization studies. As a next step the influence of the amount of the extraction reagent APDC on the recoveries of trace elements was studied in order to choose the minimum required amount taking into the account the degree of extraction of matrix element. The results in Table 2 are presented as recoveries for the trace elements obtained when AAS measurement in the organic phase is carried out immediately after extraction (1 min) or after 2.5 hours.

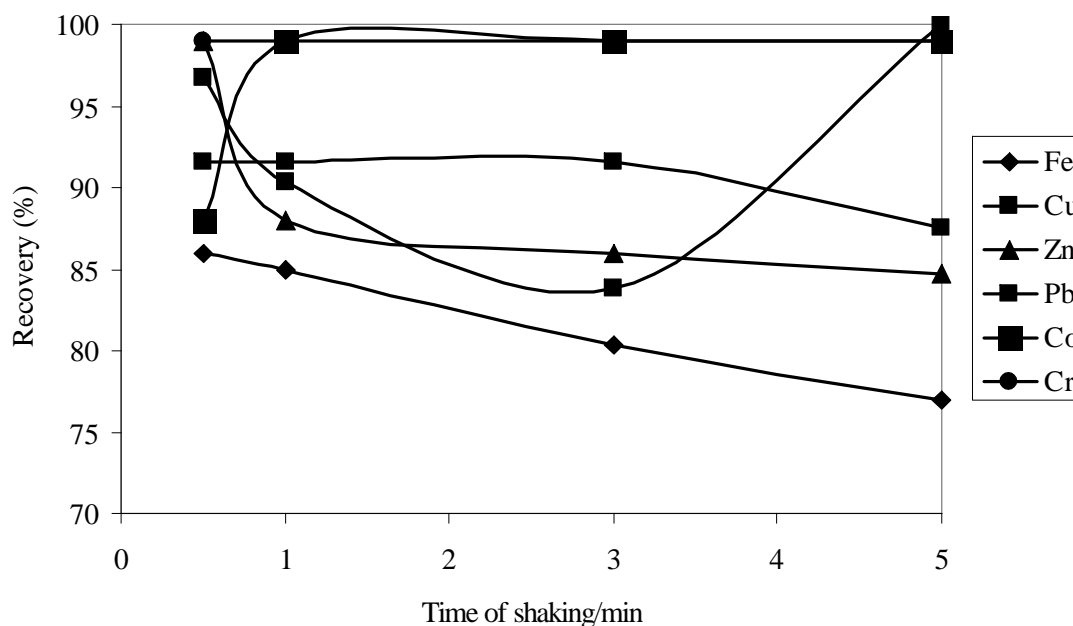
**Table 2.** Influence of the amount of APDC on the recoveries of trace elements

APDC, mg	Time	Recovery, %					
		Fe	Cu	Zn	Pb	Co	Cr(VI)
2	1 min	$57\pm 4$	$86\pm 3$	$62\pm 4$	$97\pm 2$	$65\pm 4$	$75\pm 4$
2	2.5 h	-	-	$71\pm 4$	>99	-	$85\pm 3$
5	1 min	$97\pm 2$	$98\pm 1$	$97\pm 2$	$97\pm 2$	$82\pm 3$	>99
5	2.5 h	>99	>99	>99	>99	>99	>99
10	2.5 h	$97\pm 2$	$91\pm 2$	$85\pm 3$	$98\pm 2$	>99	>99

The AAS measurement of trace elements in the organic phase immediately after extraction is impossible if 10 mg APDC is used due to strong interferences from matrix element extracted. However after 2.5 h  $\text{Mn(PDC)}_2$  is reextracted in the aqueous phase and trace elements could be determined. As can be seen 5 mg APDC is optimal amount of extraction reagent ensuring quantitative recoveries for all studied elements.

### 3.3. Extraction time

The degrees of extraction of trace elements in the presence of matrix element in dependence on the extraction time are shown in Figure 1. As it can be seen, the extraction of trace elements is more efficient using short extraction times because of the lower influence of  $\text{Mn(PDC)}_2$  presented in the organic phase. The dithiocarbamate complexes of the trace elements are formed and extracted before  $\text{Mn(PDC)}_2$  because of its lowest stability constant. As might be expected, the quantity of the extracted Mn is proportional to the shaking time and interference free determination of trace elements is ensured with as low as possible extraction time – 1 min is accepted as optimal. The time for the reextraction of  $\text{Mn(PDC)}_2$  was also optimised taking into account possible losses of trace elements which might be also coreextracted with manganese. Experiments performed showed that 2.5 h are enough for almost complete reextraction of Mn without any losses for the microelements.



**Fig. 1.** The recoveries for Co, Cr, Cu, Fe, Pb and Zn in the presence of  $\text{MnCl}_2$  depending on the extraction time

### 3.4. The amount of Mn salt

The influence of the mass of manganese sample was studied in order to achieve the highest possible preconcentration factor. Different masses of Mn salts were tested: 200 mg; 300 mg and 500 mg. The results obtained showed recoveries in the range 95-99 % for all studied elements for Mn salts of 200 mg or 300 mg. Lower recoveries for all studied microelements were observed for 500 mg manganese sample. At this case reextraction time for  $\text{Mn(PDC)}_2$  was prolonged however this leads to losses of trace elements due to corextraction.

### 3.5. Trace elements determination

ETAAS or FAAS (procedure A) are most suitable instrumental methods for trace elements determination in the organic phase obtained after matrix ( $\text{Mn(PDC)}_2$ ) reextraction. In this way all analytical steps are performed in one analytical vessel thus avoiding any possibilities for contaminations or losses of trace elements. In order to avoid measurements in organic phase and to make preconcentration procedure suitable also for ICP-AES instruments two modifications were studied: procedure B (reextraction of trace elements in  $3 \text{ mol L}^{-1} \text{ HNO}_3$ ) and procedure C (DIPE as organic solvent, evaporation of organic phase followed by dissolution of dry residue in  $3 \text{ mol L}^{-1} \text{ HNO}_3$ ).

Results for the recoveries of trace elements obtained according to procedure B and procedure C are presented in Table 3.

**Table 3.** Recoveries, % for Fe, Cu, Zn, Pb, Cr and Co in the presence of 300 mg manganese salts

Sample	Organic phase	Procedure	R (%)					
			Fe	Cu	Zn	Pb	Cr(VI)	Co
MnCl <sub>2</sub> ·4H <sub>2</sub> O	DIPE	C	>99	25±4	80±4	82±5	72±5	<1
MnCl <sub>2</sub> ·4H <sub>2</sub> O	IBMK	B	>99	>99	>99	>99	>99	>99
MnSO <sub>4</sub> ·H <sub>2</sub> O	DIPE	C	>99	25±5	>99	30±6	73±5	<1
MnSO <sub>4</sub> ·H <sub>2</sub> O	IBMK	B	>99	>99	>99	>99	>99	>99

Evidently IBMK is the most suitable solvent for the simultaneous extraction of dithiocarbamate complexes of microelements and matrix element. Recoveries higher than 99% were obtained only for Fe if DIPE is used as organic solvent. Back reextraction of trace elements in nitric acid is preferable analytical procedure for ICP-AES determination of trace elements.

### 3.6. Analytical figures of merit

The accuracy and precision of the recommended procedure A is verified by the added/found method - exact amounts of trace elements (close to their content in Mn-salt) were added to the Mn salts and determined. The quantification of trace elements in the organic phase was against calibration curve using organic dithiocarbamate standards prepared according to the procedure: known amounts of aqueous standards of trace elements are diluted till 20 mL with doubly distilled water in extraction cylinder, 1 mL acetate buffer and 0.5 mL 1% *m/V* APDC are added and extraction is performed for 1 min in 10 mL IBMK. The organic phase obtained is used as organic standard for the quantification of trace elements. Results obtained for the analysis of MnCl<sub>2</sub> are presented in Table 4.

**Table 4.** Determination of Co, Pb, Cr, Cu, Zn and Fe in MnCl<sub>2</sub>·4H<sub>2</sub>O (procedure A, n=3)

Element	Added, µg g <sup>-1</sup>	Found, µg g <sup>-1</sup> (mean±s)	RSD, %	Recovery
Co	0.49	0.51±0.03	5.8	104
Cr	0.87	0.88±0.04	4.5	101
Cu	0.93	0.94±0.05	5.3	101
Fe	12.1	11.6±0.2	1.3	95.9
Pb	0.87	0.95±0.04	4.2	109
Zn	12.1	12.1±0.2	1.7	99.6

Additionally, comparative analyses of parallel samples were performed according to the recommended procedure A and ETAAS determination of trace elements after sample dissolution in H<sub>2</sub>O. Very good agreement as can be seen from Table 5 was found thus confirming the validity of the developed procedure for the analysis of Mn-salts. The detection limits achieved depend on the instrumental method used for trace elements measurement. For recommended procedure A and ETAAS as instrumental method they are: 0.01 µg g<sup>-1</sup> for Co, Cr, Cu and 0.02 µg g<sup>-1</sup> for Fe and Pb. For Zn, usually determined by FAAS detection limit attained is 0.01 µg g<sup>-1</sup>. Relative standard deviation varied in the range from 2 to 12% (ETAAS determination, procedure A) for all studied elements at levels of content from 0.04 to 1 µg g<sup>-1</sup>

**Table 5.** Analysis of MnSO<sub>4</sub>·H<sub>2</sub>O (n=3)

Element	Recommended procedure A (mean±s) µg g <sup>-1</sup>	ETAAS (sample dissolved in H <sub>2</sub> O) (mean±s) µg g <sup>-1</sup>
Co	0.24±0.01	0.22±0.01
Cr	0.64±0.02	0.65±0.03
Cu	0.86±0.04	0.81±0.03
Fe	8.5±0.3	8.2±0.2
Pb	0.46±0.02	0.48±0.02
Zn	2.8±0.2	2.9±0.1

#### 4. Conclusion

Analytical method for the determination of Co, Cr, Cu, Fe, Pb and Zn in manganese salts was developed. The preconcentration and separation procedure is based on the simultaneous extraction of dithiocarbamate complexes of trace elements and matrix element Mn and their different kinetics of reextraction. The proposed analytical procedure is a simple, sensitive and accurate method for the preconcentration of trace elements from manganese salts and could be combined with ETAAS, FAAS and ICP-AES measurement of trace elements. The procedure developed is applied to the analysis of high purity MnCl<sub>2</sub> and MnSO<sub>4</sub>. However it can be used for the analysis of all type of manganese salts.

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