

REPORT

No. 2094

**THE DETERMINATION, BY ATOMIC-ABSORPTION
SPECTROPHOTOMETRY, OF IMPURITIES IN
MANGANESE DIOXIDE**

by

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ANALYTICAL CHEMISTRY DIVISION

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IMPURITIES IN MANGANESE DIOXIDE

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SYNOPSIS

This report describes various methods for the determination of impurities in electrolytic manganese dioxide by atomic-absorption spectrophotometry (AAS).

The sample is dissolved in a mixture of acids, any residue being ignited and retreated with acid. Several AAS methods were applied so that the analysis required to meet the specifications could be attained. These involved conventional flame AAS, AAS with electrothermal atomization (ETA), hydride generation coupled with AAS, and cold-vapour AAS. Of the elements examined, copper, iron, zinc, and lead can be determined direct with confidence with or without corrections based on recoveries obtained from spiked solutions. Nickel can be determined direct by use of the method of standard additions, and copper, nickel, and lead by ETA with the method of standard additions. Arsenic and antimony are determined by hydride generation coupled with AAS, and mercury by cold-vapour AAS. The precision of analysis (relative standard deviation) is generally less than 0,050.

Values were obtained for aluminium, molybdenum, magnesium, sodium, copper, chromium, and cadmium, but the accuracy of these determinations has not been fully established.

SAMEVATTING

Hierdie verslag beskryf verskillende metodes vir die bepaling van onsuiverhede in elektrolitiese mangaandioksied deur atoomabsorpsiespektrofotometrie (AAS).

Die monster word in 'n suurmengsel opgelos en enige residu word verbrand en met suur behandel. Verskeie AAS-metodes is toegepas om die ontleding wat aan die spesifikasies sal voldoen, te kry. Hierdie metodes het die konvensionele vlam-AAS, AAS met elektrottermiese verstuiwing (ETA), hidriedontwikkeling met AAS gekoppel en kouedamp-AAS ingesluit. Van die elemente wat ondersoek is, kan koper, yster, sink en lood met vertroue regstreeks bepaal word met of sonder korreksies wat gebaseer is op herwinnings wat met gesoute oplossings verkry is. Nikkel kan regstreeks met gebruik van die metode van standaardbyvoegings bepaal word en koper, nikkel en lood deur ETA met die metode van standaardbyvoegings. Arseen en antimoon word bepaal deur hidriedontwikkeling met AAS gekoppel en kwik deur kouedamp-AAS. Die presisie van die ontleding (relatiewe standaardafwyking) is gewoonlik minder as 0,050.

Waardes is vir aluminium, molibdeen, magnesium, natrium, koper, chroom en kadmium bepaal, maar die akkuraatheid van hierdie bepalings is nog nie behoorlik vasgestel nie.

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1. INTRODUCTION

The National Institute for Metallurgy (NIM) is currently engaged on an investigation into the production of pure electrolytic manganese dioxide from furnace byproducts. Electrolytic manganese dioxide is used in industry, for example in the manufacture of batteries. To be internationally competitive, the manganese dioxide produced in South Africa must meet certain specifications for a number of trace constituents. The Japanese specifications for electrolytic manganese dioxide are given in Table 1.

TABLE 1

Lower limits of determination and specifications

Analyte	Method of measurement	LLD $\mu\text{g/g}$	Japanese specification $\mu\text{g/g}$	Analyte	Method of measurement	LLD $\mu\text{g/g}$	Japanese specification $\mu\text{g/g}$
Al	AAS-MoA	50	10	Hg	CV	0,5	10
As	AAS-HG	0,3	3	Mg	AAS-MoA	5	10
Ca	AAS-MoA	10	10	Mo	ETA	1	2
Cd	ETA	0,2	10	Na	AAS-MoA	10	10
Co	ETA	0,5	8	Ni	ETA	0,5	5
Cr	ETA	0,5	10	Pb	ETA	1	10
Cu	AAS	5	3	Sb	AAS-HG	0,2	1
Fe	AAS	20	20	Zn	AAS	5	10

AAS = flame atomic-absorption spectrophotometry

MoA = method of standard additions

HG = hydride generation

ETA = electrothermal atomization

CV = cold-vapour AAS

LLD = lower limit of determination

The literature^{1,2} describes methods for the determination of trace elements in manganese by flame atomic-absorption spectrophotometry (AAS) after the manganese matrix has been separated from the other constituents. This ensures that a satisfactory degree of sensitivity and of freedom from background interference are obtained. The separation, which is accomplished by adsorption onto activated charcoal, when tested in the laboratory at NIM, was found to be inadequate in the presence of relatively large amounts of iron. Besides, only a limited number of elements could be determined. Optical emission spectrometry using inductively coupled plasma as the source of excitation also requires separation of the manganese matrix from the impurities so that spectral interference from the manganese³ is excluded.

In view of these difficulties, it was decided that NIM should undertake an investigation into the applicability of flame AAS to the direct measurement of trace elements in the presence of manganese and, where necessary, into the use of alternative techniques such as electrothermal atomization (ETA), hydride generation, and cold-vapour AAS.

2. EXPERIMENTAL METHOD

Certain factors must be considered in the choice of a suitable flame procedure. These include choice of a suitable method of dissolution, assessment of the degree of interference from the manganese, and classification of the analytes into three groups: those that can be determined direct, those that can be determined after further dilution, and those that can be determined by use of the method of standard additions. Consideration must then be given to the use of alternative AAS approaches, e.g., hydride generation for elements that are insensitive to the normal flame (e.g., arsenic and antimony), ETA for elements that may be present in the low parts-per-million or smaller range, and the cold-vapour technique for mercury.

It was decided that no attempt would be made to determine silicon and titanium by flame AAS since the method is very insensitive for these elements. Although it seemed unlikely that aluminium and molybdenum could be determined successfully by flame AAS at the level required in the Japanese specifications, they were determined by this technique in the present investigation.

2.1. Apparatus

The atomic-absorption instrument used was a Varian Techtron model AA475 spectrophotometer fitted with a Varian Techtron carbon-rod atomizer, CRA 90, and hollow-cathode lamps. A Varian chart

recorder, model 9176, was used to record the ETA peaks. The apparatus used for hydride generation and for the cold-vapour determination of mercury is described elsewhere^{1,5}.

2.2. Dissolution of the Sample

For complete dissolution of the sample, the acids used should oxidize the organic material and volatilize the silica. In addition, the simultaneous use of hydrofluoric and perchloric acids (which results in the loss of arsenic) should be avoided.

The usual procedure for the dissolution of manganese dioxide by digestion with hydrochloric or nitric acids^{1,2,6} did not completely dissolve the samples submitted for analysis. It was concluded that part of the residue consisted of carbon since, after the acid solution had been evaporated to dryness, ignition at 800°C reduced the mass of the residue.

Fusion of the sample or the residue with sodium carbonate or peroxide was not considered suitable. The reason was twofold: firstly, sodium was one of the analytes and, secondly, fusion would necessitate considerable dilution of the sample and an unacceptable loss of sensitivity. The following dissolution technique was therefore adopted. A sample of 5 g was digested in hydrochloric acid, the solution was filtered, and the filter paper containing the undissolved residue was ashed. This ashed residue was treated twice with hydrofluoric acid and taken to dryness. It was then dissolved in a 1:4 mixture of nitric and perchloric acids, and again fumed to dryness. The residue was dissolved in aqua regia. This solution and the filtrate from the earlier step were combined, evaporated to incipient dryness, dissolved in a mixture of 5 ml of hydrochloric acid and 1 ml of nitric acid, and made up to volume in a 50 ml volumetric flask. Further dilutions were made, according to the concentration levels of the analytes, with 10 per cent hydrochloric acid.

2.3. Measurement by Flame AAS

The dissolution of a 5 g sample of high-purity manganese dioxide in 50 ml of solution results in a solution with a manganese concentration of 60 g/l. It was therefore considered necessary for the interference level of this matrix on the analytes to be investigated. In the absence of a reference material with reliable values, the level of interference could be established only by the addition of known quantities of each analyte to a different portion of the sample after dissolution, as shown in Table 2. The amounts of the analytes added to two sample solutions after the appropriate dilutions were calculated to give absorbance readings that were twice and four times as high respectively. The spiked and unspiked samples were measured against pure calibration standards, matched with respect only to concentration and type of acid. In an attempt to minimize any interference, a nitrous oxide-acetylene flame was used wherever possible (Table 3). The average recovery* from the spiked solutions are shown in Table 2, from which it can be concluded that, at the given dilutions, aluminium, iron, molybdenum, lead, and zinc are the only analytes that can be measured against pure calibration standards, since, at the concentration levels determined, the mean recoveries from the spiked solutions are within approximately 5 per cent of the amount of element added. Of the others, copper, calcium, cadmium, and sodium can be determined if a correction is made for the recovery since this is relatively high (84 to 94 per cent), although elimination of the interference would be preferable. The recoveries of cobalt, magnesium, and nickel are so low that these analytes can be determined only by use of the method of standard additions to correct for the observed interferences. Because of its extremely low recovery from the spiked solution, chromium requires determination by an alternative approach such as ETA. Although high blank values were encountered in the determination of calcium, magnesium, and sodium, these do not necessarily invalidate these conclusions since reproducible recoveries from the spiked solutions were obtained for two separate additions. However, if adequate corrections are omitted for these blank values, a bias could be introduced that would affect the calculated recoveries from the spiked solutions.

Matrix interference can be corrected for either by the use of matched standards or by the method of standard additions. The first approach was not possible in this investigation since no suitably pure source of manganese was available, and recourse was therefore made to the second possibility.

2.4. Measurement by Flame AAS with the Method of Standard Additions

A further series of determinations by the method of standard additions was carried out for aluminium, calcium, magnesium, sodium, nickel, and lead in four samples of manganese dioxide. The plotted absorbance readings gave straight lines for all the analytes, indicating that this approach is possible for these elements when they are present in low concentrations. The dilutions used were the same as those given in Table 2 for the recoveries from spiked solutions.

*In this report, recovery means amount determined as a percentage of the amount added.

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TABLE 2

Recovery of added analyte by flame AAS

Sample no.	Analyte	Analyte concn in unspiked sample mg/l	Dilution factor	Recovery %
2	Al	117	20	104
4		109	20	106
2	Ca	70	125	95
4		72	125	93
2	Cd	0,1	15	84
4		0,1	15	84
2	Co	2	15	56
4		2	15	50
2	Cr	8	15	23
4		6	15	42
2	Cu	18	50	95
4		6	50	90
2	Fe	1480	200	98
4		92	200	98
2	Mg	12	125	62
4		33	125	60
2	Mo	7	25	99
4		1	25	102
2	Na	540	500	84
4		340	500	89
2	Ni	2	20	65
4		1	20	63
2	Pb	11	25	98
4		26	25	91
2	Zn	28	125	94
4		39	250	100

TABLE 3

Instrumental parameters for flame AAS

Analyte	Dilution factor	Wavelength nm	Spectral bandwidth nm	Type of flame	Fuel	Background correction
Al	20	309,3	0,5	N ₂ O ₂ -C ₂ H ₂	Rich	No
Ca	100	422,7	0,5	N ₂ O ₂ -C ₂ H ₂	Rich	No
Cu	50	324,8	0,5	C ₂ H ₂ -air	Lean	No
Fe	100	248,3	0,2	N ₂ O ₂ -C ₂ H ₂	Lean	Yes
Mg	100	285,3	0,5	C ₂ H ₂ -air	Lean	Yes
Na	100	589,0	0,5	C ₂ H ₂ -air	Lean	No
Zn	100	213,9	1	C ₂ H ₂ -air	Lean	Yes
Ni	100	232,0	0,5	C ₂ H ₂ -air	Lean	Yes

2.5. Measurement by Electrothermal Atomization

In an attempt to obtain confirmatory results and to test an alternative technique for the measurement of elements present in low concentrations, two samples were analysed by ETA for as many analytes as possible. The ETA technique with the method of standard additions that had been used previously for the analysis of cobalt, copper, nickel, and lead, in electrolytic manganese was used in the present work for the measurement of these elements and cadmium, chromium, and molybdenum. The instrumental parameters are given in Table 4.

TABLE 4

Instrumental parameters for electrothermal atomization

Standard conditions:

Drying temperature 100°C Atomization time 1 s
 Drying time 30 s Ramp rate 800°C/s

Analyte	Wavelength nm	Background correction	Ashing		Atomization temperature °C
			Temp. °C	Time s	
Cd	228,8	Yes	400	25	1600
Cr	357,9	No	900	20	2300
Mo	313,3	No	1500	20	2500
Cu	324,8	No	900	25	2200
Co	240,7	Yes	900	25	2200
Ni	232,0	Yes	1000	20	2200
Pb	283,3	Yes	450	25	2200

Further dilutions were necessary, thus reducing the matrix effects still further. The residual matrix effects were corrected for by the method of standard additions. The measurement by ETA of aluminium was unsuccessful owing to the appearance of double peaks during atomization.

2.6. Hydride-generation and Cold-vapour Techniques

After the sample had been dissolved as described in Section 2.2, a hydride-generation technique^{5,6} was used with the method of standard additions on a very dilute sample solution for the determination of arsenic and antimony in the solutions by AAS. Mercury was measured by use of cold-vapour AAS¹ after the sample had been dissolved as described earlier.

3. LOWER LIMITS OF DETERMINATION

The lower limits of determination, i.e., the concentrations at which the precision of the measurement is not expected to exceed 5 per cent, are given in Table 1 with the specification limits quoted by Japanese sources. These limits are not achieved for all the elements by any one method but by a combination of four, viz, flame AAS, ETA, hydride generation and AAS, and cold-vapour AAS. These specification limits can be met for all the analytes except aluminium.

4. RESULTS AND DISCUSSION

4.1. Precision and Accuracy Based on Recoveries from Spiked Solutions

The precision and accuracy of the method, based on the recoveries from spiked solutions, are shown in Table 5 for five of the elements, and in Table 6 for four of the elements. This work was limited to one element by each of the different AAS techniques because of the time available and the limited amount of sample solution. The precision test is based on the results obtained from ten different portions of the sample, and the accuracy test on the recovery from a solution that was spiked before the sample was dissolved, the addition being made to four or six portions of the sample and measured relative to an unspiked sample.

TABLE 5

Comparison of the precision of the methods used

Analyte	Method	Number of determinations	R.S.D.
As	MoA-HG	10	0,037
Cu	Direct AAS*	12	0,018
Mg	MoA-AAS	10	0,047
Zn	Direct AAS*	10	0,025
Ni	ETA	7	0,14

* With correction for recovery from spiked solutions
 R.S.D. = relative standard deviation
 MoA = method of standard additions
 HG = hydride generation

TABLE 6

Comparison of the accuracy of the methods used

Analyte	Method	Number of determinations	Amount added mg/l	Mean recovery mg/l	Recovery %
As	MoA-HG	4	0,016	0,016 ($\pm 0,001$)	101
Cu	Direct AAS*	6	0,60	0,59 ($\pm 0,012$)	98
Mg	MoA-AAS	4	0,192	0,188 ($\pm 0,010$)	98
Zn	Direct AAS*	6	0,128	0,121 ($\pm 0,016$)	98

* With correction for recovery from spiked solutions
 MoA = method of standard additions
 HG = hydride generation

It appears that the relative standard deviation of the AAS procedure, except that for ETA, lies between 0,018 and 0,050, and that the recoveries of the very small additions can be regarded as being adequate. The relative standard deviation of the ETA procedure is much higher, e.g., 0,14 for nickel.

The percentage recoveries from the spiked solutions range from 98 per cent for copper to 101 per cent for arsenic when the measuring techniques listed in Table 5 are used.

4.2. Analysis of Test Samples

The results obtained for some of the analytes by different methods are compared in Table 7. The results for the direct method corrected for the recoveries from spiked solutions and the values obtained by the method of standard additions generally show a fair measure of agreement, e.g., for calcium, magnesium, nickel, and lead. The agreement for aluminium and sodium is not good, presumably because of the low sensitivity of flame AAS for aluminium and the high blank values associated with the determination of sodium.

A comparison between the results obtained by ETA and those obtained by direct AAS with correction for the recoveries from spiked solutions (cobalt, copper, and molybdenum) or the method of standard additions (nickel and lead) show that the values for all the analytes except molybdenum are generally in good agreement. For molybdenum by the direct method, only an indication of the value was obtained for the two samples compared. It can therefore be concluded that both methods give the same order of concentration, i.e., less than 5 p.p.m. Similarly, for cadmium, no comparison of the two methods is possible since only an indication of the value was obtained.

Other elements that were determined by only one AAS technique were iron, zinc, chromium, arsenic, antimony, and mercury. The high concentration of iron (1900, 1500, 1770, and 980 $\mu\text{g/g}$ for samples 1 to 4 respectively) and the high sensitivity for zinc made it impossible for the alternative ETA technique to be

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TABLE 7

Results obtained by different procedures

Analyte	Al, $\mu\text{g/g}$				Ca, $\mu\text{g/g}$				Cd, $\mu\text{g/g}$				Co, $\mu\text{g/g}$			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Flame AAS																
Direct*	86	58	58	51	82	74	70	77	<0.2	<0.2	<0.2	<0.2	2	3.8	3.8	3.8
MoA	36	90	205	130	75	69	88	69			<0.2	<0.2			5.8	2.1
AAS-ETA IE and C	110	91	105	82												
Analyte	Cr, $\mu\text{g/g}$				Cu, $\mu\text{g/g}$				Mg, $\mu\text{g/g}$				Mo, $\mu\text{g/g}$			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Flame AAS																
Direct*					9.7	19.8	6.5	6.5	14	19	45	55	9	7	<5	<5
MoA							8	6.5	35	23	45	54			2.4	3.1
AAS-ETA IE and C			2.9	1.4									7	7	17	4
ASV					2	16	3	4					9	9	13	3
Analyte	Na, $\mu\text{g/g}$				Ni, $\mu\text{g/g}$				Pb, $\mu\text{g/g}$				Zn, $\mu\text{g/g}$			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Flame AAS																
Direct*	97	460	1070	370	1.1	2	2	1.4	48	16	10	35	24	28	13	39
MoA	75	77	778	210	1.7	3.4	3.4	1.8	38	17	12	28				
AAS-ETA							2.6	1.9			8	30				
ASV													20	26	9	41

* Corrected where necessary according to the recovery from the spiked solution

MoA = method of standard additions

IE and C = ion exchange and colorimetry

ASV = anodic-stripping voltammetry

used. Because of the high recoveries (98 to 100 per cent) from the spiked solutions, it was not necessary for the method of standard additions to be adopted for these two elements.

The low concentration of chromium and its susceptibility to interference in the flame meant that this analyte could be determined only by ETA. The values obtained by this approach for samples 3 and 4 were 2.9 and 1.4 $\mu\text{g/g}$ respectively (Table 7). Arsenic, antimony, and mercury had to be determined by special techniques as a result of their low concentrations (average values of 11 $\mu\text{g/g}$, 0.5 $\mu\text{g/g}$, and less than 0.5 $\mu\text{g/g}$ respectively) and their poor sensitivity in the flame. As shown in Table 6, the recovery of arsenic from a spiked manganese solution resulted in a recovery of 100 per cent by AAS with hydride generation. The dilutions for antimony and mercury are high, and it can therefore be assumed that interferences from the matrix will be small. Because the method of standard additions was also used, there is no reason why these determinations should be any less accurate than those for arsenic.

In an attempt to confirm the values obtained by AAS techniques or to establish values where none could be obtained by AAS (e.g., for titanium), use was made of anodic-stripping voltammetry (ASV) and of ion exchange coupled with spectrophotometric techniques. The elements determined by ASV after the sample had been digested in acid were cadmium, copper, molybdenum, and zinc. Titanium, aluminium, and molybdenum were determined by spectrophotometry after complete dissolution of the sample and ion-exchange separation. This last approach was verified by recoveries from spiked solutions in the presence of manganese. (Difficulty is experienced in the determination, by any AAS technique, of these elements when they are present in trace concentrations.)

The ASV results generally confirm the levels of concentration determined by AAS for copper, zinc, and molybdenum, although there are considerable differences for copper and molybdenum in one of the four samples analysed. The ASV values for cadmium in sample 1 (and possibly sample 4) are significantly different from the AAS values.

The values obtained by the spectrophotometric method after ion-exchange separation do not support the AAS values for aluminium, but, like the ASV results, they confirm the AAS values for molybdenum except for sample 3. Here, the ASV and colorimetric results (ion-exchange separation) agree. The sample

masses used in these two methods (0.1 g for ASV and 1.0 g for colorimetry) are much smaller than the 5 g used for AAS. Nevertheless, the duplicate results by these methods do not vary sufficiently to account for these differences. The values obtained for titanium after ion-exchange separation were 20 to 50 $\mu\text{g/g}$, i.e., much lower than could possibly be determined by AAS methods.

From the data available, it is evident that the determination, by AAS techniques, of aluminium and possibly molybdenum is unsatisfactory; that the concentration of titanium is too low for this element to be determined by AAS; that more attention should be given to the determination of magnesium, sodium, and calcium in regard to the control of blank values, to the determination of chromium by ETA (on which little information is available), and to confirmation of the AAS values for cadmium. Not all the samples that were subsequently examined dissolved completely by the proposed dissolution technique. In these instances, a combustion step is essential to remove graphite, but it results in losses of arsenic and mercury. Combustion would simplify and shorten the dissolution procedure, and the problem caused by the presence of the arsenic and the mercury could be overcome by the preparation of a separate sample solution (by fusion) for their determination by hydride generation and AAS and by cold-vapour AAS; this is not possible for the other trace constituents (Section 2.2).

The time taken for the analysis (including the dissolution) of a batch of 12 samples is 7 days with an elapsed time of 8 days for the determination of 12 constituents.

5. CONCLUSIONS AND RECOMMENDATIONS

It was found that, provided the concentrations are sufficiently high, copper, iron, zinc, molybdenum, aluminium, and lead can be determined direct by flame AAS without significant interference from the manganese matrix, the error being not more than 5 per cent relative. The determination of calcium, nickel, sodium, and magnesium requires the method of standard additions. Where they are present in low concentrations, cadmium, cobalt, chromium, nickel, lead, and molybdenum can be determined by AAS with ETA coupled with the method of standard additions, whereas hydride generation-AAS and cold-vapour AAS are essential for the determination of arsenic, antimony, and mercury.

Although the various AAS methods are sufficiently sensitive for the specification limits to be met for all the elements under consideration, only cobalt, copper, nickel, lead, iron, zinc, arsenic, antimony, and mercury can be determined with confidence, and the accuracy of the results for some elements, e.g., aluminium, molybdenum, magnesium, sodium, calcium, chromium, and cadmium must be questioned, especially for the last five elements mentioned. The determination, by one or other of the AAS techniques, of aluminium and molybdenum at the concentrations in question is not recommended, nor is the determination of silicon and titanium. Further modification of the dissolution procedure should be considered.

The precision of analysis (relative standard deviation) for the elements considered is less than 0.050, except for the ETA procedure. All the methods investigated are lengthy.

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APPENDIX

**THE DETERMINATION, BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY, OF TRACE
ELEMENTS IN ELECTROLYTIC MANGANESE DIOXIDE
(LABORATORY METHOD NO. 0/21)**

1. OUTLINE

The sample is dissolved in a mixture of hydrochloric, nitric, perchloric, and hydrofluoric acids, and is measured by various techniques involving atomic-absorption spectrophotometry (AAS), as follows: arsenic and antimony by hydride generation; mercury by cold vapour; cobalt, nickel, and lead (depending on their concentrations) by the method of standard additions with electrothermal atomization (ETA); nickel, aluminium, calcium, sodium, and magnesium by the method of standard additions with flame atomization; and copper, iron, and zinc by conventional flame measurement with or without corrections based on the recoveries from spiked solutions. If the concentration levels of molybdenum and lead are sufficiently high, conventional flame atomization can be used.

2. APPLICATION OF THE METHOD

The method is applicable to the determination of traces of cobalt, copper, nickel, lead, iron, zinc, arsenic, antimony, and mercury in manganese dioxide. Elements such as aluminium, molybdenum, magnesium, sodium, calcium, chromium, and cadmium can also be determined, but the accuracy of the method for these elements has not been fully established.

This procedure should also be applicable to the determination of trace elements in manganese ores.

3. APPARATUS**(1) Varian Techtron Atomic-absorption Spectrophotometer Model AA475**

Fitted with hollow-cathode lamps for flame measurements, and coupled with a Varian Techtron carbon-rod atomizer CRA 90 for ETA.

(2) Varian Techtron Atomic-absorption Spectrophotometer Model AA6

Coupled with a hydride-generation vessel^{1,2}. Used for the measurement of arsenic, antimony, and mercury.

4. REAGENTS**(1) Hydrochloric Acid**

A.R. grade.

(2) Perchloric Acid

A.R. grade.

(3) Nitric Acid

A.R. grade.

(4) Potassium Nitrate, 100 g/l

Dissolve 10 g of KNO_3 in triply distilled water and dilute to 100 ml.

(5) Potassium Biphthalate, 20 g/l

Dissolve 2 g of $\text{KHC}_8\text{H}_4\text{O}_4$ in triply distilled water and dilute to 100 ml.

(6) Lanthanum, 10 per cent (v/v)

Dissolve 24.7 g of $\text{La}(\text{NO}_3)_3$ in triply distilled water and dilute to 100 ml.

(7) Standard Solutions for Calibration

1 mg/l.

Prepare these solutions as described in the Varian Techtron manual³. Obtain calibration standards for measurement by diluting the 1 mg/l solutions with appropriate acids and reagents (Table I-1).

5. PROCEDURE**5.1. Dissolution of the Sample**

- a. Accurately weigh about 5 g of sample into a 250 ml Phillips beaker. Slowly add 20 ml of concentrated hydrochloric acid, and cover with a watch-glass, allowing the reaction to subsi¹ before heating gently on a hot-plate for 20 minutes.

IMPURITIES IN MANGANESE DIOXIDE

- b. Cool, and filter the solution through a no. 541 Whatman filter paper. Ash the filter paper containing the undissolved residue in a porcelain crucible over a Bunsen burner, and transfer the ash to a 100 ml Teflon beaker.
- c. Treat the residue with 10 ml of hydrofluoric acid and fume to dryness. Add 5 ml of nitric acid and 20 ml of perchloric acid, and again fume to dryness.
- d. Add 15 ml of aqua regia and heat on a hot-plate until all the residue has dissolved (Note 1). Combine this solution with the hydrochloric acid filtrate from step b, and take to near dryness before diluting to 50 ml with 10 per cent (v/v) hydrochloric acid and 2 per cent (v/v) nitric acid.

TABLE I-1

Standard solutions for calibration

Analyte	Medium	Range, mg/l	Calibration method
Al	10% HCl and 1% KNO ₃	0, 3, 6, 12	MoA
Ca	5% HNO ₃ and 1% La	0, 1, 2, 3	MoA
Cu	10% HCl and 1% KNO ₃	0, 0,2, 0,5, 1, 2, 3, 4, 5	S St
Fe	10% HNO ₃ and 1% KNO ₃	0, 4, 10, 15, 20, 25, 30, 40	S St
Mg	10% HNO ₃ and 1% KNO ₃	0, 0,2, 0,4, 0,6	MoA
Na	2% HNO ₃ and 0,2% KHC ₈ H ₄ O ₄	0, 0,6, 1,2, 1,8	MoA
Zn	10% HNO ₃	0, 0,1, 0,2, 0,4, 0,6, 0,8, 1	S St
Ni	10% HNO ₃	0, 1, 2, 3	MoA

MoA = method of standard additions

S St = synthetic standards

6. MEASUREMENT

6.1. Conventional Flame Atomization

- a. After suitable dilution of the sample solution (Table I-2), measure copper, iron, and zinc against synthetic standards.
- b. For copper, spike the solution with copper, and correct the result accordingly.
- c. For aluminium, calcium, magnesium, sodium, and nickel, use the method of standard additions (Table I-1).

TABLE I-2

Instrumental parameters for flame AAS

Analyte	Dilution factor	Wavelength nm	Spectral bandwidth nm	Type of flame	Fuel	Background correction
Al	20	309,3	0,5	N ₂ O ₂ -C ₂ H ₂	Rich	No
Ca	100	422,7	0,5	N ₂ O ₂ -C ₂ H ₂	Rich	No
Cu	50	324,8	0,5	C ₂ H ₂ -air	Lean	No
Fe	100	248,3	0,2	N ₂ O ₂ -C ₂ H ₂	Lean	Yes
Mg	100	285,3	0,5	C ₂ H ₂ -air	Lean	Yes
Na	100	589,0	0,5	C ₂ H ₂ -air	Lean	No
Zn	100	213,9	1	C ₂ H ₂ -air	Lean	Yes
Ni	100	232,0	0,5	C ₂ H ₂ -air	Lean	Yes

6.2. Electrothermal Atomization

- a. Condition the rod (Note 2) for all the elements by firing the concentrated sample solution twenty times before the analysis.
- b. Use the conditions and instrumental parameters listed in Table I-3 for cobalt, copper, nickel, lead, cadmium, chromium, and molybdenum.
- c. Use the special carbon-rod slit for all the elements, and argon as the purge gas.

TABLE I-3

Instrumental parameters for electrothermal atomization

Standard conditions:

Drying temperature 100 °C Atomization time 1 s
 Drying time 30 s Ramp rate 800 °C/s

Analyte	Wavelength nm	Background correction	Ashing		Atomization temperature °C
			Temp. °C	Time s	
Cd	228,8	Yes	400	25	1600
Cr	357,9	No	900	20	2300
Mo	313,3	No	1500	20	2500
Cu	324,8	No	900	25	2200
Co	240,7	Yes	900	25	2200
Ni	232,0	Yes	1000	20	2200
Pb	283,3	Yes	450	25	2200

6.2.1. Preparation of Chromium Solutions

- a. Dilute 2 ml of the original sample solution (Section 5.1) to 25 ml with 2 per cent (v/v) nitric acid.
- b. Transfer four 4 ml aliquot portions of the diluted solution into 20 ml flasks.
- c. Add 0 ml, 0,05 ml, 0,1 ml, and 0,15 ml of 5 mg/l chromium solution and dilute to volume with 2 per cent nitric acid. This represents additions of 0 mg, 0,0125 mg, 0,025 mg, and 0,0375 mg of chromium per litre.

6.2.2. Preparation of Molybdenum Solutions

- a. Dilute 2 ml of the original sample solution (Section 5.1) to 25 ml with 2 per cent (v/v) nitric acid.
- b. Transfer four 4 ml aliquot portions of diluted solution to 25 ml volumetric flasks.
- c. Add 0 ml, 0,1 ml, 0,2 ml, and 0,3 ml of 2 g/l molybdenum solution and dilute to volume with 2 per cent (v/v) nitric acid. This represents additions of 0 mg, 0,008 mg, 0,016 mg, 0,024 mg of molybdenum per litre.

6.2.3. Preparation of Cadmium Solutions

- a. Dilute 9 ml of the original solution (Section 5.1) to 25 ml with 2 per cent (v/v) nitric acid.
- b. Transfer four 4 ml aliquot portions of diluted solution to 25 ml volumetric flasks.
- c. Add 0 ml, 0,1 ml, 0,2 ml, and 0,3 ml of 2 mg/l cadmium solution and dilute to volume with 2 per cent (v/v) nitric acid. This represents additions of 0 mg, 0,008 mg, 0,016 mg, and 0,024 mg of cadmium per litre.

6.3. Measurement of Arsenic and Antimony with Hydride Generation

Use the method of standard additions, following the procedure described elsewhere^{2,4}.

6.4. Measurement of Mercury by Cold-vapour AAS

Use the method of standard additions under the conditions set out elsewhere¹.

7. CALCULATION

- a. For the method of standard additions, plot the average peak height (or absorbance in flame measurement) versus the concentration of the element added.
- b. Extrapolate the line connecting the four points back to the x-axis, and read off the concentration of the element in milligrams per litre.
- c. Multiply the value read off by the dilution factor to obtain the concentration in the original sample.

8. NOTES

- (1) Any residue remaining probably consists of carbon or graphite, and ignition of this residue may be necessary to give complete dissolution. However, during this process, antimony, arsenic, and mercury will be lost, and a fresh portion of sample material (1 g) must be fused with 4 g of sodium peroxide in zirconium crucibles, leached in 20 per cent (v/v) hydrochloric acid, and diluted to 100 ml for the determination of arsenic, antimony, and mercury.
- (2) For reliable, precise, and consistent peak heights to be obtained, the rod must be conditioned by the firing of 5 μ l portions of the original sample solution twenty times.

9. REFERENCES

1. ROBERT, R.V.D., and STEELE, T.W. Atomic-absorption determination, in metal sulphide concentrates, of the elements that form gaseous hydrides. Johannesburg, National Institute for Metallurgy, *Report 1838*. 1976. 38 pp.
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3. VARIAN TECHTRON. Analytical methods for flame spectroscopy. Australia, Varian Techtron, *Manual*.
4. ROBERT, R.V.D. The determination of mercury by cold-vapour atomic-absorption spectrophotometry. Randburg, National Institute for Metallurgy, *Report 1872*. 1977. 17 pp.