

A NEW POLAROGRAPHIC METHOD FOR DETERMINING TRACES OF MANGANESE SUSPENDED IN INDUSTRIAL ATMOSPHERES

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INTRODUCTION

The toxic effects of manganese in various industries have become important from the point of view of industrial medicine. This has led us to seek a more sensitive method for determining this toxic element in industrial environments. Industries concerned are the metallurgical and iron and steel, and also those engaged in the manufacture of glass, paint, varnish, and electric batteries; the soldering industry can be included since the rods used often contain manganese.

Most of the analyses carried out nowadays for this purpose use colorimetric methods, which consist in oxidizing manganese to the permanganate state and comparing the resulting characteristic coloration with that of previously prepared standards. Among these methods we may mention that of Willard and Greathouse¹⁻³, in which the oxidation is carried out with sodium or potassium periodate; others use ammonium persulphate as the oxidizing agent in the presence of silver ions as catalyst³⁻⁵.

Considering the great accuracy and sensitivity of the polarographic method, we, for our part, have looked for, and, we think, found, a method which gives greater precision, working at low concentrations, than colorimetric methods.

Various studies of the polarographic behaviour of manganese exist; some authors⁶⁻⁸ used alkaline and alkaline-earth chlorides as supporting solutions with small quantities of gelatine to suppress maxima; others recommended ammonium salts⁹⁻¹¹ as supporting solutions; others again used potassium sulphocyanide⁶⁻¹² or potassium cyanide¹³. In all these cases, when great sensitivity is desired, the oxygen in the working solutions must be eliminated in order to avoid possible interference by the cathode reduction waves of oxygen.

In a previous publication¹⁴ we pointed out that manganese exhibited a cathodic reduction wave at very low concentrations when using 0.1N sodium sulphite as a supporting solution. This procedure avoids the necessity of eliminating the oxygen in the test solutions by means of a current of purified hydrogen or nitrogen; the sulphite, acting as a strong reducing agent, eliminates the oxygen in the solutions, and at the same time acts as a support favouring the diffusion currents of the ions under study.

In the experiments reported here we used accordingly 0.1N sodium

sulphite as a supporting solution. The experiments showed that manganese exhibits its cathodic reduction wave (whose height or diffusion current is proportional to the concentration of manganese) not only when the latter is tested alone, but also when tested in the presence of such elements as phosphorus, cadmium, copper, arsenic, lead, calcium, and iron, with which it is often associated in industrial samples.

A comparative study is also presented with the commonest colorimetric method (oxidation to permanganate with ammonium persulphate), and the polarographic method is shown to be more accurate and more sensitive.

Finally, to prove the efficiency of the method which we propose, previously prepared samples were analysed by the polarographic technique and the errors shown not to exceed 5 per cent.

EXPERIMENTAL PROCEDURE

Apparatus

The polarograph used was a Type PO3 Radiometer with a graphic recorder, a drop-electrode as cathode with a velocity of 20 drops per minute, and a saturated calomel electrode as anode.

A Lange's Medico-Photocolorimeter with blue filter (BG7) was used in the colorimetric studies.

Sensitivity

The polarograph was used with a sensitivity of $S = 1/10$, that is, a tenth of the total sensitivity of the recording galvanometer, duly calibrated so that a displacement of 1 mm of the indicator needle corresponded to a diffusion intensity of $I_d = 4 \times 10^{-9}A$.

Reagents

The products used were all Merck's reagents for analysis, with redistilled water.

Supporting solution

In all the experiments we used a supporting solution of 0.1N sodium sulphite prepared three or four hours before the experiment. This supporting solution served a double purpose: first, it acted as a support favouring the the diffusion currents of the cations; second, it acted as a reducing agent, and so destroyed the oxygen dissolved in the test solutions. Thus the interferences which may be caused by the polarographic waves of the oxygen are eliminated, these being very marked at such high sensitivities. We thus avoided the necessity of eliminating the oxygen by the usual device, which consists in passing a current of hydrogen or purified nitrogen through the solutions for 20 or 30 minutes. The sodium sulphite must be crystallized and of the highest quality, *i.e.*, it must not have been exposed to the air, and must not present the appearance of having been oxidized to sulphate, so that it will not have lost its reducing power—otherwise it cannot destroy all the oxygen in the test solutions. Nor must sulphite solutions be used which have been prepared long before the experiment.

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Standard solutions

To prepare the standard solution of manganese we took very pure potassium permanganate, dissolved it in water and then acidified the solution with sulphuric acid. The permanganate was reduced by adding a solution of concentrated oxalic acid drop by drop until complete decoloration was obtained. This solution was diluted with water to a fixed volume, a stock solution being thus obtained with a concentration of 0.1 mg/ml of manganese. From this another was prepared with a concentration of 10 $\mu\text{g/ml}$ of manganese, which was used in all the experiments. In making this solution, it was necessary to bear in mind that, using a supporting solution of sulphite, one cannot add solutions of high acidity, since they decompose the sulphite and sulphur dioxide is given off; the latter would interfere since it is characterized polarographically by two waves, and so before the solution was gauged it had to be neutralized with 1N ammonia to, pH 5.0.

The solutions of the other elements, in whose presence the polarographic analysis of manganese was carried out, were prepared from the following compounds, and at the concentrations given:

<i>Compounds</i>	<i>Elements</i>
Na ₂ HPO ₄	P= 100 $\mu\text{g/ml}$
Cd(NO ₃) ₂	Cd= 100 $\mu\text{g/ml}$
CuSO ₄	Cu= 100 $\mu\text{g/ml}$
As ₂ O ₅	As= 100 $\mu\text{g/ml}$
Pb(NO ₃) ₂	Pb= 100 $\mu\text{g/ml}$
CaCl ₂	Ca= 100 $\mu\text{g/ml}$
Fe(NO ₃) ₃	Fe= 100 $\mu\text{g/ml}$

POLAROGRAPHIC BEHAVIOUR

Manganese

Using a supporting solution of 0.1N sodium sulphite, the polarographic behaviour of manganese alone was studied, and it was observed that the cathodic reduction wave was manifested at a half-wave potential of $E_{\frac{1}{2}} = -1.54$ volt in relation to the saturated calomel electrode (S.C.E.); concentrations between 0.5 and 5 $\mu\text{g/ml}$ were tested, which gave polarographic waves (Figure 1), whose diffusion intensities are given in Table 1. These values are represented graphically as a function of the concentrations in Figure 2; a perfectly linear relationship is observed.

Table 1. Manganese $t=22^\circ\text{C}$.

<i>Concentrations</i> ($\mu\text{g/ml}$)	<i>I_d</i> ($\mu\text{A} \times 10^{-2}$)
0.5	3.41
1.0	6.60
2.0	13.20
3.0	20.40
4.0	27.20
5.0	35.10

Manganese polarogram.

Supporting soln Na_2SO_3 0.1N

Sensitivity = 1/10

Velocity = 20 drops/min

Temperature = 20°C.

Wave height = 1 mm, $I_d = 4 \cdot 0 \times 10^{-3} \mu\text{A}$

1st Supporting soln

4th Conc = 2.0 $\mu\text{g/ml}$
 $I_d = 13.2 \times 10^{-2} \mu\text{A}$

5th Conc = 3.0 $\mu\text{g/ml}$
 $I_d = 20.4 \times 10^{-2} \mu\text{A}$

6th Conc = 4.0 $\mu\text{g/ml}$
 $I_d = 27.2 \times 10^{-2} \mu\text{A}$

7th Conc = 5.0 $\mu\text{g/ml}$
 $I_d = 35.1 \times 10^{-2} \mu\text{A}$

2nd Conc = 0.5 $\mu\text{g/ml}$
 $I_d = 3.41 \times 10^{-2} \mu\text{A}$

3rd Conc = 1.0 $\mu\text{g/ml}$
 $I_d = 6.6 \times 10^{-2} \mu\text{A}$

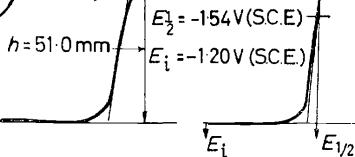


Figure 1

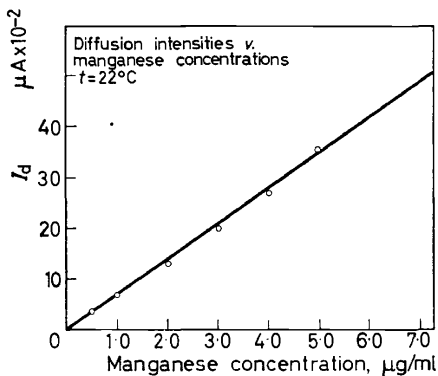


Figure 2

PHOTOCOLORIMETRIC BEHAVIOUR

We followed the procedure of Snell and Snell¹⁵, which consists in oxidizing manganese salts to permanganate in the presence of silver ions with ammonium persulphate at 80°C. Working with the same concentrations as were tested polarographically, we obtained the values in Table 2, measured with the blue filter (BG 7). From Figure 3 it is observed that there is a greater departure from a linear relationship than with the polarographic results. The method is also less sensitive; whereas in the photocolourimeter, for the maximum concentration tested (5 $\mu\text{g/ml}$), the extinction value observed is 0.085, corresponding to only 18 per cent absorption, in the case of the polarogram, for this same concentration, the wave height is 88 mm, the maximum displacement of the needle being 100 mm. Whence we deduce

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that the polarographic method shows greater sensitivity and accuracy for manganese, at these low concentrations, than the photocolourimetric method.

Table 2. Photocolourimetry of manganese

Concentrations ($\mu\text{g/ml}$)	Extinctions
1.0	0.020
2.0	0.032
3.0	0.060
4.0	0.077
5.0	0.085

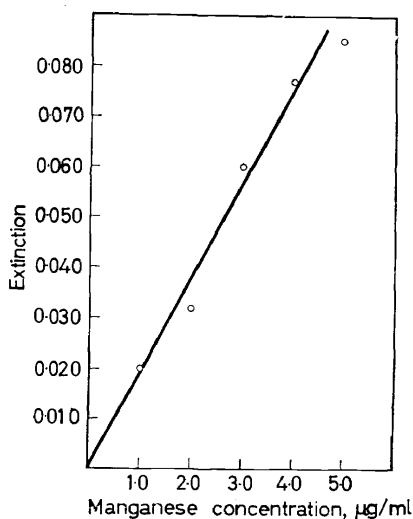


Figure 3

Manganese in the presence of other elements Cd, Cu, As, Pb, Ca, Fe, and phosphates

In the same way as with manganese alone, a polarographic study of this element was carried out in the presence of cadmium, copper, arsenic, lead, calcium, iron and phosphates in constant concentrations higher than that of manganese. The polarographic recording was begun at a potential of $E_i = -1.2\text{V}$, so as to prevent the manifestation of any waves proper to these elements. First, each of them was tested separately, then they were all tested together. The values obtained are given in *Tables 3-14*, and the corresponding graphs in *Figures 4 and 5*.

As may be observed, in all cases there is a perfectly linear relationship between the diffusion intensities recorded and the manganese concentrations tested, whence we deduce that none of the elements studied causes interference in the polarographic determination of manganese, even where a

slight clouding or precipitate is observable in the solution in the polarographic cell, as when lead and calcium were tested in the presence of PO_4H^{2-} , SO_4^{2-} , and SO_3^{2-} ions.

Table 3. Manganese in the presence of 10 $\mu\text{g}/\text{ml}$ of P

Concentrations ($\mu\text{g}/\text{ml}$)	I_d ($\mu\text{A} \times 10^{-2}$)
0.5	4.0
1.0	6.8
2.0	13.6
3.0	20.8
4.0	27.4
5.0	35.2

Table 4. Manganese in the presence of 10 $\mu\text{g}/\text{ml}$ of Cd

Concentrations ($\mu\text{g}/\text{ml}$)	I_d ($\mu\text{A} \times 10^{-2}$)
0.5	2.6
1.0	5.2
2.0	12.0
3.0	19.8
4.0	26.8
5.0	35.0

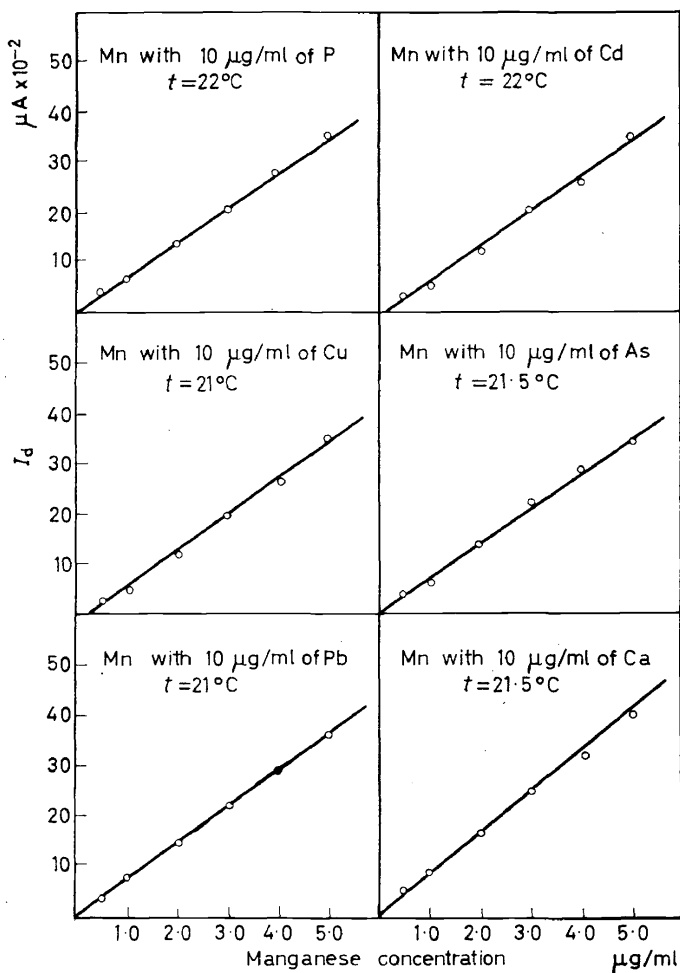


Figure 4

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Table 5. Manganese in the presence of 10 µg/ml of Cu

Concentrations (µg/ml)	I_d ($\mu A \times 10^{-2}$)
0.5	2.0
1.0	5.2
2.0	12.0
3.0	19.6
4.0	26.8
5.0	34.8

Table 6. Manganese in the presence of 10 µg/ml of As

Concentrations (µg/ml)	I_d ($\mu A \times 10^{-2}$)
0.5	3.4
1.0	6.8
2.0	14.0
3.0	21.2
4.0	28.0
5.0	34.2

Table 7. Manganese in the presence of 10 µg/ml of Pb

Conclusions (µg/ml)	I_d ($\mu A \times 10^{-2}$)
0.5	3.6
1.0	7.6
2.0	14.6
3.0	21.6
4.0	29.2
5.0	36.4

Table 8. Manganese in the presence of 10 µg/ml of Ca

Conclusions (µg/ml)	I_d ($\mu A \times 10^{-2}$)
0.5	4.0
1.0	8.0
2.0	16.0
3.0	24.0
4.0	32.0
5.0	40.0

Table 9. Manganese in the presence of 10 µg/ml of Fe

Conclusions (µg/ml)	I_d ($\mu A \times 10^{-2}$)
1.0	7.2
2.0	14.2
3.0	20.8
4.0	27.6
5.0	36.0

Table 10. Manganese in the presence of 5 µg/ml each of P and Ca

Conclusions (µg/ml)	I_d ($\mu A \times 10^{-2}$)
0.5	3.8
1.0	7.6
2.0	16.0
3.0	23.2
4.0	31.2

Table 11. Manganese in the presence of 5 µg/ml each of P, Ca, As and Fe

Conclusions (µg/ml)	I_d ($\mu A \times 10^{-2}$)
0.5	3.6
1.0	7.0
2.0	14.2
3.0	21.6
4.0	28.4

Table 12. Manganese in the presence of 5 µg/ml each of P, Ca, As, Fe and Cd

Conclusions (µg/ml)	I_d ($\mu A \times 10^{-2}$)
0.5	3.4
1.0	6.4
2.0	13.0
3.0	19.4
4.0	26.4
5.0	33.4

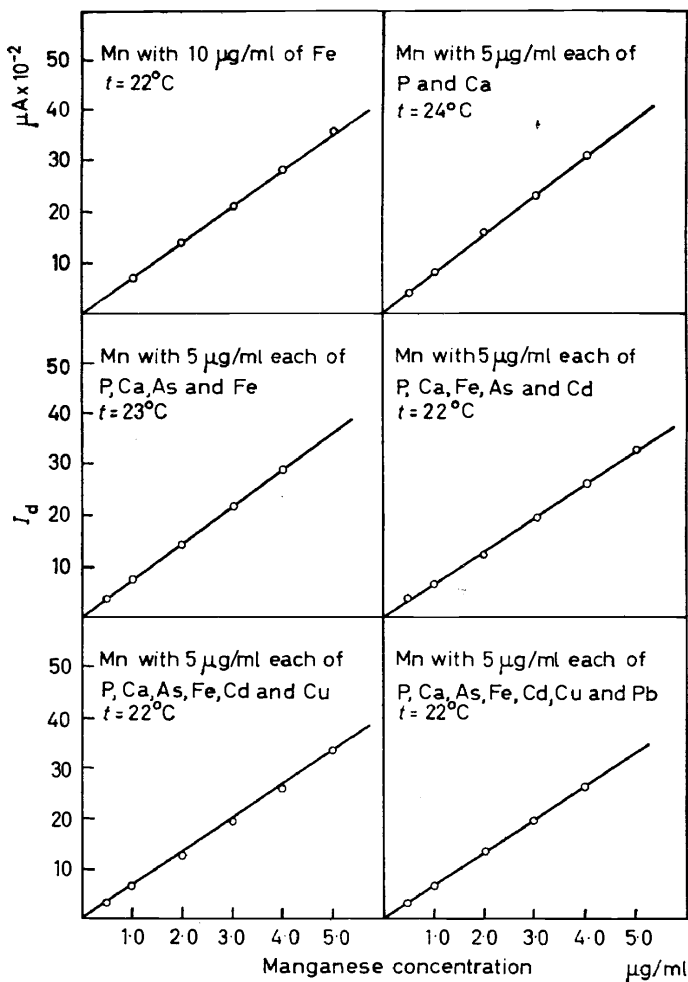


Figure 5

Table 13. Manganese in the presence of 5 µg/ml each of P, Ca, As, Fe, Cd and Cu

Conclusions (µg/ml)	I_d ($\mu A \times 10^{-2}$)
0.5	3.4
1.0	6.4
2.0	12.8
3.0	19.4
4.0	26.0
5.0	33.4

Table 14. Manganese in the presence of 5 µg/ml each of P, Ca, As, Fe, Cd, Cu and Pb

Conclusions (µg/ml)	I_d ($\mu A \times 10^{-2}$)
0.5	3.4
1.0	6.8
2.0	14.0
3.0	20.4
4.0	26.4

POLAROGRAPHIC ANALYSIS OF STANDARD SAMPLES

In order to prove the efficiency and accuracy of the polarographic method for the determination of manganese, standard samples were analysed. The

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method of polarographic evaluation followed was that of wave increases which has been explained in a former publication¹⁰; the following 3 waves were obtained:

First wave—The supporting solution was put into the polarographic cell, with a known quantity of the sample, and the corresponding polarographic wave was found; this served as a standard for measuring the wave increases of the next two.

Second wave—A known quantity of the test sample was added to a similarly prepared cell and the corresponding wave was found.

Third wave—To the cell prepared as for the measurement of the first wave, a known quantity of the standard solution of manganese was added.

It is, of course, preferable that these three waves should be obtained by testing identical volumes in the polarographic cells so as to avoid having to make corrections for volume; the diffusion current increases of the second and third waves with respect to the first are compared, and the concentration of the sample is deduced therefrom (it has been proved that the diffusion current and the concentration are always strictly proportional). This method of evaluation has the advantage, compared with the use of standard curves, of eliminating the need for an exact temperature control during the experiments. The three polarographic waves required for the evaluation of the sample were obtained in the space of a few minutes, and, therefore, without any appreciable variations of temperature. In *Figure 6* the three polarographic waves used in the evaluation of Sample 5 are given.

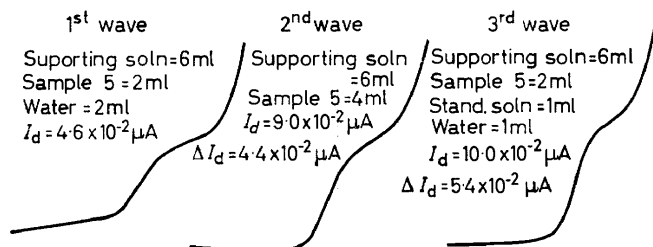


Figure 6

In *Table 15* the results obtained from the ten samples are given. It will

Table 15. Sample analysed

Sample	P ($\mu g/$ ml)	Ca ($\mu g/$ ml)	As ($\mu g/$ ml)	Fe ($\mu g/$ ml)	Cd ($\mu g/$ ml)	Cu ($\mu g/$ ml)	Pb ($\mu g/$ ml)	Mn added ($\mu g/$ ml)	Mn found ($\mu g/$ ml)	Differ- ence ($\mu g/$ ml)	Error (%)
1	12.5	12.5	—	12.5	—	12.5	—	5.00	4.80	-0.20	-4.0
2	12.5	—	12.5	—	12.5	—	12.5	5.00	4.85	-0.15	-3.0
3	11.1	11.1	11.1	—	—	—	11.1	5.55	5.40	-0.15	-2.7
4	11.1	—	11.1	11.1	11.1	11.1	—	4.45	4.50	+0.05	+1.1
5	15.0	—	15.0	20.0	—	—	10.0	4.00	4.07	+0.07	+1.7
6	8.7	12.5	12.5	—	8.7	8.7	—	5.00	4.87	-0.13	-2.6
7	16.6	6.6	3.3	6.6	3.3	3.3	3.3	6.66	6.35	-0.31	-4.7
8	13.3	13.3	6.6	13.3	6.6	6.6	6.6	3.33	3.40	+0.07	+2.1
9	5.0	6.5	5.5	10.0	5.0	4.5	7.5	8.80	7.85	-0.95	-10.8
10	10.0	5.0	7.5	5.5	5.0	7.5	7.5	2.50	2.57	+0.07	+2.8

be seen that there is excellent agreement between the quantities of manganese which were put into the samples and the amounts found by this polarographic method of evaluation; in no case did the errors exceed 5 per cent. This proves that none of the elements added in higher or lower concentrations than that of manganese interferes in the determination of this element.

EXPERIMENTAL TECHNIQUE FOR THE POLAROGRAPHIC DETERMINATION OF MANGANESE IN FUMES AND DUST

The samples of fumes and dust must be collected by the recognized "Impinger" techniques: electrostatic precipitator, thermic precipitator, filtration, *etc.*, or by any other method of high efficiency. The sample is dissolved in a small volume of 10 per cent nitric acid, the solution is evaporated to dryness on a hot water-bath, and the dried residue is dissolved in a few ml of 0.1N hydrochloric acid. This solution is neutralized with 0.1N ammonia to pH 4.0, and it is diluted to exactly 10.0 ml. From this diluted solution a known part is taken for the polarographic evaluation, on a supporting solution of 0.1 N sodium sulphite, Na_2SO_3 , using the wave increase method already described.

The amounts put into the polarographic cell may be the following (they can, of course, be varied according to the concentration of manganese in the samples):

The first wave is obtained with 6 ml of supporting solution, 2 ml of the sample and 2 ml of water.

The second wave with 6 ml of supporting solution and 4 ml of the sample

The third wave is obtained with 6 ml of supporting solution, 2 ml of the sample, 1 ml of the standard solution and 1 ml of water.

The diffusion intensity increases of the second and third waves in relation to the first are measured, and from these increases the concentration of manganese in the test sample is calculated.

CONCLUSIONS

(1) Manganese, on a supporting solution of 0.1N sodium sulphite, is characterized by a cathodic reduction wave at a half-wave potential of $E_{\frac{1}{2}} = -1.54\text{V}$ in relation to the S.C.E. at 22°C. Using this supporting solution, the oxygen in solution does not interfere since it is quickly eliminated.

(2) There is a perfectly linear relationship between the concentration of manganese tested, 0.5–5 $\mu\text{g}/\text{ml}$, and the diffusion intensities. This polarographic method is shown to be more sensitive and accurate, working at low concentrations, than the photocolometric method involving oxidation to permanganate, which is generally used to determine manganese.

(3) There is no interference in the polarographic determination of manganese, by cadmium, copper, arsenic, lead, calcium, iron or phosphates, whether in higher or lower concentrations than those of manganese.

(4) Analyses of standard samples prove that polarographic method is accurate when increases of the diffusion intensity are used instead of the standard curves for the evaluation; the errors never exceed 5 per cent.

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(5) This method can be used with great efficacy for the determination of manganese in dust and fumes on account of its great sensitivity and accuracy, and also because the elements with which it may be associated in the samples do not interfere.

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