

## Complexometric Determination of Magnesium in Manganese-containing Aluminium Alloys

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By the determination of magnesium in aluminium alloys magnesium was titrated with EDTA in the presence of manganese masked as the hexacyanomanganate(III). The logarithmic stability constant for the hexacyanomanganate(III) complex is estimated to be 28. The accuracy of the method was compared with that of a gravimetric method. No systematic deviation was shown to exist between the two methods. The standard deviation was found to be 0.0094 % Mg. In the present paper, the titration and masking is theoretically discussed on the basis of conditional stability constants and side reaction coefficients.

Several methods for the titration of magnesium in aluminium alloys with EDTA and DCTA have been reported.<sup>1-6</sup> Generally, interference of manganese may be avoided by precipitation of the magnesium as the hydroxide, while the manganese remains in the solute state as cyanomanganate (I, II, or III). According to the method proposed by Birtel,<sup>1</sup> both manganese and magnesium are present as divalent ions before the final titration. A thorough investigation of the procedure showed, however, that manganese under the conditions applied was not masked satisfactorily and thus was partly titrated. Because of this the indicator change from blue to red was not permanent.

Provonda and Pribil<sup>2</sup> have titrated calcium and magnesium with EDTA in a solution where manganese was masked as hexacyanomanganate(III). A slightly modified procedure is applied for the analysis of magnesium in manganese-containing aluminium alloys. According to Provonda and Pribil Mn(II) in cyanide solution is only slowly transformed to Mn(III) by oxidation with air. Using hydrogen peroxide small amounts of Mn(II) in cyanide solution immediately are oxidized to Mn(III) cyanide.

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The stability constant for the Mn(III) complex is not known with certainty,<sup>7</sup> but from data in the literature, it is possible to make a useful estimation of it and on this basis to draw the conclusion that manganese may be effectively masked as manganese(III) with cyanide.

#### ANALYSIS METHOD

The method proposed in this paper involves no filtrations of liquid containing cyanide, the manganese being masked with cyanide immediately before the final titration. Trace of aluminium is masked with triethanolamine. Adapted to practical conditions, the revised procedure is as follows:

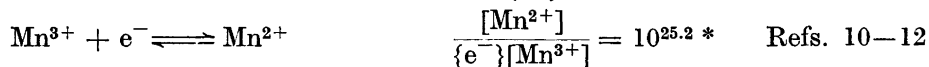
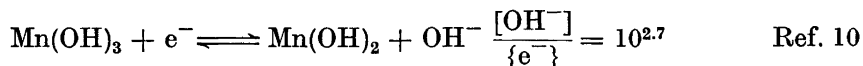
Two grams of metal drillings are dissolved in 20 ml 8 M NaOH. When the formation of hydrogen has ceased, 10 ml 3 % (w/v) hydrazine sulphate and 100 ml hot water are added. The solution is boiled for 2 min and then filtered through a medium filter. The residue is washed with hot water, and redissolved with 50 ml 6 M HCl. The filtrate is collected and subsequently is made up to 250 ml with water in a volumetric flask. An aliquot of 25 ml is pipetted into a conical flask and the following reagents are added in order, the flask being shaken after each addition:

1. 20 ml buffer mixture (65 g ammonium chloride + 450 ml 25 % ammonia solution diluted with water to 1 litre),
2. 20 ml 15 M sodium cyanide,
3. 1 drop 30 % hydrogen peroxide,
4. 10 ml 25 % (v/v) triethanolamine,
5. 1–2 ml indicator (0.1 g eriochrome black T + 2 g hydroxyammonium chloride dissolved in 100 ml methanol).

Then the solution is titrated with 0.01 M EDTA (3.723 g EDTA-Na<sub>2</sub>·2H<sub>2</sub>O dissolved and diluted with water to 1 litre) until the last trace of red colour has just disappeared.

#### STABILITY CONSTANT FOR Mn(CN)<sub>6</sub><sup>3-</sup>

*Solubility product for Mn(OH)<sub>3</sub>.* The solubility product  $S_{\text{Mn(OH)}_3}$  is calculated on the basis of the equilibrium constants for the following reactions, the redox equilibrium expressions formulated according to Ref. 8. Where possible the constants applied have been corrected to 0.1 ionic strength.<sup>9</sup>



\* This equilibrium was investigated in 7.5 M H<sub>2</sub>SO<sub>4</sub> and according to Latimer<sup>10</sup> there is a large unknown correction for the activities. This may affect the stability constant of the hexacyanomanganate(III) complex. Since the stability constant of the Mn(III)EDTA complex used is based on this same value, the calculated conditional constants are not affected.

Solving this system of equations in regard to  $[\text{Mn}^{3+}][\text{OH}^-]^3$  yields  $S_{\text{Mn}(\text{OH})_3} = 10^{-34.9}$ .

*Hydrolysis constant for  $\text{Mn}(\text{CN})_6^{3-}$ .* Meyer<sup>20</sup> determined the degree of hydrolysis of  $\text{K}_3\text{Mn}(\text{CN})_6$  titrating the amount of precipitated manganese(III) hydroxide with oxalic acid.



Assuming that  $\text{Mn}(\text{CN})_6^{3-}$  is the predominant complex it is possible to calculate the hydrolysis constant

$$K_h = \frac{[\text{HCN}]^3 [\text{CN}^-]^3}{[\text{Mn}(\text{CN})_6^{3-}]}$$

Table 1 summarizes Meyer's measurements with recalculated results. (Meyer's treatment involving some miscalculations led him to a diverging value for the hydrolysis constant of about  $10^{-10}$ ). The average value of the last column is  $-\log K_h = 7.6$ . From this

$$K_{\text{Mn}(\text{CN})_6^{3-}} = \frac{K_{\text{H}_2\text{O}}^3}{K_h \cdot S_{\text{Mn}(\text{OH})_3} \cdot K_{\text{HCN}}^3} = \frac{(10^{-14})^3}{10^{-7.6} \times 10^{-34.9} \times (10^{-9.2})^3} = 10^{28}$$

Table 1. Calculation of the stability constant of the hexacyanomanganate(III) complex. The concentrations are expressed in mole/litre,  $C$  standing for the stoichiometric concentration.

Experiment No.	$C_{\text{KMn}(\text{CN})_6}$	$C_{\text{KCN}}$	[Hydrolyzed]	$[\text{Mn}(\text{CN})_6^{3-}]$	$[\text{CN}^-]$	[HCN]	$-\log K_h$
1	0.00283		0.00220	0.00063	0.00660	0.00660	9.9
2	0.00686		0.00354	0.00332	0.01062	0.01062	9.3
3	0.01010		0.00392	0.00618	0.01176	0.01176	9.4
4	0.08730		0.00818	0.07912	0.02454	0.02454	8.6
5	0.1730		0.0179	0.1551	0.0537	0.0537	6.8
6	0.2542		0.0198	0.2344	0.0594	0.0594	6.8
7	0.004488	0.2007	0.0022	0.002288	0.2073	0.0066	5.9
8	0.007842	0.3549	0.0014	0.006442	0.3591	0.0042	6.3
9	0.02379	0.5772	0.0008	0.02299	0.5796	0.0024	6.9
10	0.06423	0.5772	0.0011	0.06313	0.5808	0.0033	7.0
11	0.09274	0.9234	0.0007	0.09204	0.9255	0.0021	7.1
12	0.22990	0.9234	0.0010	0.2289	0.9264	0.0030	7.0

Table 2 lists stability constants at an ionic strength of approximately 0.1. For the hexacyanomanganate(III) complex, the estimated value is used, while the other stability constants are taken from the literature.<sup>13,21</sup>

#### CONDITIONAL CONSTANTS

In the present analysis, aluminium is separated as aluminate from magnesium hydroxide by filtration. Apart from  $\text{Mn}(\text{II})$  all ions which might be

Table 2. Logarithmic cumulative stability constants for complexes with  $n$  ligands.

$\log \beta_n$	EDTA $n$	CN $n$
Mg(II)	8.7 1	
Mn(II)	13.8 1	
Mn(III)	24.5 1	28 6

present in analysis of aluminium alloys will either follow aluminium in the separation or become masked with cyanide during the titration. In the analysis of an alloy with a content of 2.0 % Mg and 0.5 % Mn according to the procedure mentioned above the solution (100 ml) will at the end point be composed as shown in Table 3.

Table 3. Initiatory number of moles per 100 ml and concentrations of reaction products.

	Mole $\times 10^3$		M $\times 10^3$
Magnesium	0.165	MgEDTA	1.65
Manganese	0.018	Mn(CN) $_6^{3-}$	0.18
EDTA	0.165	NH $_3$	972
Sodium cyanide	30	NH $_4$	468
Hydrogen chloride	30	CN $^-$	228
Triethanolamine	17	HCN	72
Ammonium chloride	24	(HOCH $_2$ CH $_2$ ) $_3$ N	170
Ammonia	120	H $_2$ O $_2$	5
Hydrogen peroxide	0.5	Cl $^-$	540
		Na $^+$	300

Based on the values of HCl, NH $_4$ Cl, NH $_3$ , and NaCN and with a logarithmic acid constant of  $-9.37$  for NH $_4^+$  and  $-9.20$  for HCN, the concentrations of the reaction products are calculated. The pH of the solution is calculated to be 9.70.

Table 4. Side reaction coefficients and conditional constants for Mn(III)EDTA and Mg(II)EDTA by adding a) 10 ml, and b) 20 ml cyanide.

	A	B	[B]	$\log \alpha$	$\log Ky'y'$
a	Mn(III)	CN $^-$	0.110	22.3	1.4
	Mn(II)				7.9
	EDTA	H $^+$	$10^{-9.64}$	0.8	
b	Mn(III)	CN $^-$	0.228	24.1	$-0.4$
	Mg(II)				7.9
	EDTA	H $^+$	$10^{-9.70}$	0.8	

Table 4 shows side reaction coefficients and conditional constants for Mg(II) and Mn(III) at two different cyanide concentrations, that is, addition of 10 ml and 20 ml sodium cyanide solution, respectively. The calculations are performed according to Ringbom:

$$K_{ML'} = K_{ML}/(\alpha_{M(CN)}\alpha_{L(H)}) \quad (\text{Ref. 14})$$

$$\alpha_{Mn(CN)} = [CN]^6 \times K_{Mn(CN)_6} \quad (\text{Ref. 15})$$

$$\alpha_{L(H)} = 10^{0.8} \text{ at pH} = 9.7 \quad (\text{Ref. 16})$$

From the last column, it is seen that the conditional constants for Mn(III)EDTA at both cyanide concentrations are less than  $10^2$ , which is normally the condition for satisfactory masking. It was found, however, that the end point was stable only when 20 ml sodium cyanide solution was used. This might be due to a reaction between Mn(III) and the indicator.

#### TITRATION ERROR

At pH = 9.70 the colour change<sup>17</sup> for eriochrome black T is at  $pMg_{trans} = 5.1$ . A calculation of the magnesium concentration at the equivalence point<sup>18</sup> gives:

$$pMg_{eq} = (pC_{Mg} + \log K_{MgY})/2 = (2.78 + 8.7)/2 = 5.7$$

From this it is possible to calculate<sup>19</sup> the theoretical titration error  $F$ .

$$\Delta pMg = pMg_{trans} - pMg_{eq} = 5.1 - 5.7 = -0.6$$

and

$$F = (10^{\Delta pMg} - 10^{-\Delta pMg})/(C_{MgY'})^{\frac{1}{2}} = -1.0 \%$$

At the transition point 50 % of the indicator remains attached to the magnesium. When the titration is carried out until the last trace of red colour has just disappeared, the titration error will be very close to zero.

#### ANALYSIS RESULTS

Various aluminium alloys have been analysed both after the method mentioned above and after a gravimetric method.<sup>6</sup> As previously the sample is dissolved with sodium hydroxide. After oxidation with hydrogen peroxide the precipitate will consist of magnesium hydroxide and manganese dioxide. The precipitate is dissolved in acid. Manganese is precipitated as dioxide with bromine in ammoniacal solution. From the filtrate magnesium is precipitated as ammonium phosphate, ignited to pyrophosphate and then weighed. The results are collected in Table 5.

The absolute standard deviation of the titrimetric method based on the results of sample Nos. 2–6 is calculated as 0.0094 % Mg with a 95 % upper confidence limit of 0.021 % Mg. This result is also born out by the regular use in industrial practice. A comparison of the titrimetric procedure with that or gravimetry reveals no essential systematic deviation between the two methods.

Table 5. Magnesium determinations in manganese-free and manganese-containing alloys.

Sample No.	% Mn	% Mg gravimetric	% Mg titrimetric
1	1.5		0—0
2	0	0.55—0.55	0.52—0.55
3	0	0.81—0.85—0.81—0.85	0.85—0.86
4	0	0.55—0.56	0.56—0.55—0.56—0.56
5	0.5	1.15—1.19—1.17—1.17	1.19—1.19
6	0.3	2.09—2.12	2.12—2.13

*Acknowledgements.* The author wishes to thank the directors of Northern Cable- and Wire Works and the head of the metallurgical laboratory Mr. P. Bruun for the opportunity to do this work and permission to publish. Colleagues at Chemistry Department A are thanked for valuable discussions and help in preparing the manuscript.

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Received August 11, 1967.