

## Analytical methods for RE-Co alloys

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**Abstract.** Total RE, Co and Fe in mischmetal and its cobalt alloys are determined by visual complexometric methods and instrumental x-ray fluorescence techniques. As Fe causes interference in the determinations of RE and Co and its own determination is affected by the presence of Co, it is removed by precipitation. The iron is determined from the precipitate and RE and Co from the filtrate. Accuracy of the method is checked by analysing synthetic mixtures of RE, Co and Fe. The individual REs in mischmetal are determined by x-ray fluorescence method. The analysis technique is based on comparison of the oxides of the test samples with standards (both in pressed pellet form) in the appropriate composition range. The total RE content of mischmetal determined through complexometric analysis is compared with the total RE determined through x-ray fluorescence.

**Keywords.** X-ray fluorescence technique; complexometric method; misch metal.

### 1. Introduction

Recently rare earth cobalt alloys particularly  $\text{SmCo}_5$  and  $\text{MMCo}_5$  (MM standing for mischmetal), the latter because of its lower cost, have become important permanent magnetic materials. The magnetic characteristics are considerably influenced both by the collective presence of the rare earths as well as by the relative amounts of Ce, La, Nd and Pr present in MM. In order to have a control on the composition of MM and its cobalt alloys accurate, rapid and simple methods for determination of the collective and relative amounts of these rare earths have become important.

Complexometric determination of Sm and Co in  $\text{SmCo}_5$  alloys has been reported recently by Brusdeylins (1975) and Zimkova *et al* (1973). Based on the fact that the stability constants of the four lighter rare earths namely, Ce, La, Nd and Pr are nearly the same, we present in this paper a complexometric method of determination of total RE in MM and its cobalt alloys.

X-ray fluorescence (designated hereafter as x-rf) analysis of various RE oxides in ores and in other samples has been reported by Lytle *et al* (1957), Higashi and Miyake (1975), Sasaki (1973), Chandola *et al* (1975), Tertian (1968) and Bonnevie-Svendsen and Follo (1973), but the literature on the analysis of RE in MM and its cobalt alloys is indeed limited, see Brusdeylins (1975) and Alota and Bartoli (1975). An x-rf method for the analysis of individual RE in MM, based on comparing the samples with synthetic standards approximating the composition of the samples, is reported here.

## 2. Complexometric method

### 2.1. Experimental

2.1a. *Reagents and solutions* : Xylenol orange – 0.1%, murexide – 50 mg of the indicator is ground with 1 g of NaCl to a very fine powder, sulphosalicylic acid, hexamine – 20%, EDTA – 0.01 M, Zn solution – 0.01 M.

Philips portable pH meter was used for pH measurements.

MM or its cobalt alloy was dissolved in the minimum quantity of concentrated  $\text{HNO}_3$  in a beaker, boiled and made up the solution to a known volume. If the sample contained iron the sample solution prepared in the above way was diluted to 100 ml and warmed to  $50^\circ\text{C}$  after the addition of about 5 g solid  $\text{NH}_4\text{Cl}$ . 0.5 M  $\text{NH}_4\text{OH}$  was added in drops with constant stirring till the pH increased to 4. Iron(III) hydroxide can be precipitated quantitatively from solutions of pH 4 (Ayres 1958). The contents in the breaker was boiled, precipitate was allowed to settle and filtered into a measuring flask. The precipitate was thoroughly washed with hot water and the filtrate and washings were made up to a known volume. This was used for the determinations of total RE and Co. The precipitate was dissolved in dilute HCl, made up to a known volume and used for the determination of Fe.

2.1b. *RE determination* : A known volume of solution containing between 25 and 45 mg of RE is diluted to about 100 ml and the pH adjusted to 3 by 0.5 M  $\text{NH}_4\text{OH}$ . To this, excess of EDTA was added and the pH was adjusted to 5.5–5.9 by hexamine. This was titrated against 0.01 M zinc solution to pink colour, using xylenol orange as indicator. Excess of  $\text{NH}_4\text{F}$  followed by 100–200 mg ascorbic acid was added to the resulting solution, heated to  $80\text{--}95^\circ\text{C}$ , cooled and the liberated EDTA titrated against zinc solution to pink colour. Ascorbic acid reduces  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$ , which may be formed by air-oxidation. The pH of the solution was maintained at 5.5–5.9 throughout the titration. Colour change was sharp at a pH of 5.5–5.9. Earlier workers used a pH of 5–5.5 (Pribil 1967).

To establish an optimum value of RE to be used in each titration, experiments were carried out repeatedly using 10, 20, 25, 30, 40, 45, 50 and 60 mg of synthetic RE in each aliquot. The amount of RE content to be used was found to lie between 25 and 45 mg. To study the optimum temperature for the liberation of EDTA from the RE-EDTA complex, the decomplexation was done at 30, 40, 50, 60, 70, 75, 80, 85, 90 and  $95^\circ\text{C}$ . In these experiments the RE content was kept at an optimum value of 30 mg. The average results of five experiments in each case, given below, show that a temperature between 80 and  $95^\circ\text{C}$  was found to be most satisfactory for the liberation of EDTA from the RE-EDTA complex,

Temperature	30° C	40° C	50° C	60° C	70° C	
% of RE	99.43	99.58	99.58	99.58	99.72	
Temperature	75° C	80° C	85° C	90° C	95° C	Boiled
% of RE	99.72	99.87	99.87	99.87	99.87	99.82

The average atomic weight of the MM used was calculated as 140.82 as explained later. Thus every ml of 0.01 M EDTA complexed with RE corresponds to 1.4082 mg of RE.

2.1c. *Cobalt and iron determination*: Co (10–30 mg/100 ml) was determined by direct titration with EDTA at pH 6–7 using murexide as indicator after the addition of NaF to mask Fe and Re (Zimkova *et al* 1973). Fe (10–15 mg/100 ml) is titrated with EDTA at pH 1.5 and 60–70° C using sulphosalicylic acid as indicator (Zimkova *et al* 1973).

## 2.2. Results and discussion

2.2a. *Inhomogeneity of MM*: Two sources of MM from India, namely M/s. Mischmetal and Flints Co., Alwaye, Kerala (designated as MM(F)) and Bhabha Atomic Research Centre, Bombay (designated as MM(B)) were analysed. Typical analysis of MM(F) by wt% provided by its supplier is as follows: Total RE contents 85–90, iron 6–10 and Ca, Na, Ba, etc. 1–3. The various RE distribution (by wt%) is quoted as Ce 45–50, La 20–26, Nd 15–20, Pr 4–6 and Sm 1–4. The MM(B) is quoted to be higher in RE contents with the main impurities as Fe and Ni. Both these MM were analysed for RE. In order to determine RE complexometrically in these materials, knowledge of average atomic weight of RE is essential. From the distribution of individual RE in both the MM determined by the x-rf method (given in § 3), the average atomic weights of MM (F) and MM(B) were calculated to be 140.82 and 140.73 respectively.

Three different pieces of MM(F) and one of MM(B) were analysed and the results are shown in table 1. The determinations from different parts of one piece are shown as *a, b, c, d* and *e*. The results show that in MM(F) the Fe content ranged from 6.29 to 6.86% and the RE content ranged from 90.04 to 92.04%. In MM(B) the RE content varied from 98.39 to 99.63% with the major impurities being 0.33% Fe and 0.45% Ni. The results suggest that both MM (F) and MM(B) are inhomogeneous in composition.

2.2b. *Homogenisation of MM by annealing*: MM(F) from piece 2 (where the results from two different parts are widely different, with a mean value of 90.91 and a standard deviation of 0.926) was annealed at 700° C for 24 hr. Results of the analysis from different parts of this annealed sample are given in table 1. Mean value for RE was 91.95% with standard deviation of 0.098, which shows that annealing has homogenised the sample. Mean value for Fe was 6.68% and a standard deviation of 0.026.

2.2c. *Interference of iron*: Analysis of synthetic mixtures of MM, Co and Fe showed that Fe causes interference in the determination of RE and Co and its own determination is affected by the presence of Co. In the determination of RE when

Table 1. Complexometric determination of total RE and Fe in MM.

Sample No.	Wt % RE		Standard deviation (global)	Wt % Fe		Standard deviation (global)
	Mean (local)	Mean (global)		Mean (local)	Mean (global)	
MM(F) 1	a	90.41		6.30		
	b	91.86		6.29		
	c	90.67		6.53		
	d	90.86		6.39		
	e	91.69	90.94	0.577	6.34	6.37
MM(F) 2	a	90.04		6.69		
	b	91.77	90.91	0.926	6.53	6.61
MM(F) 3	a	90.94		6.86		
	b	92.04	91.49	0.592	6.83	6.85
MM(B) 4	a	98.39				
	b	98.86				
	c	99.63				
	d	98.85		Ni 0.45%		
	e	99.42	99.04	0.455	Fe 0.33%	
MM(F) 2	annealed at 700°C for 24 hr					
	a	91.90		6.67		
	b	92.08		6.71		
	c	91.89		6.69		
d	91.94	91.95	0.098	6.67	6.68	0.026

a, b, c, d and e are analysis from different parts of the sample.

Table 2. Complexometric determination of total RE in synthetic mixtures.

Sample	Taken in mg	Found in mg		Standard deviation
		Mean (local)	Mean (global)	
Mixture of RE	A	100	99.84	
Ce : La : Nd : Pr	B	100	99.86	
= 55 : 25 : 15 : 5	C	100	99.88	99.85 0.046

Percent error : 0.15.

A, B and C are solutions prepared at different times.

the pH is increased to 3 by ammonia and then to 5.5 by hexamine (Zimkova *et al* 1973), the solution turns yellow in colour (with 5% or more of iron), probably due to the formation of a complex. This creates difficulties in the later stages of the determination. It is found that this can be overcome by adding excess of EDTA to the solution of pH 3 followed by hexamine to adjust the pH to 5.5. At pH 6, Fe is precipitated as Fe(III) hydroxide and this introduces error in the detection of the colour change from yellow to violet (NaF was added to mask Fe and RE). In the determination of Fe the detection of the colour change from purple red to colourless or greenish yellow is not possible since solutions containing Co have pink colour.

2.2d. *Synthetic MM*: Accuracy in the determination of RE was found by analysing synthetic mixtures of Ce, La, Nd and Pr in the ratio Ce : La : Nd : Pr = 55 : 25 : 15 : 5. Results in table 2 show that the mean value is 99.85 against the sample value of 100, with a standard deviation of 0.046. Thus the accuracy of the method is 0.15%.

2.2e. *Synthetic MM, Co and Fe*: Accuracy in the determinations of RE, Co and Fe in a mixture was found by analysing synthetic mixtures of MM, Co and Fe in which the iron content was kept 0, 3, 10, 25 and 50%. Results of the analysis given in table 3 show that the error of analysis is 0.2 to 0.4% for Fe, 0.1 to 0.5% for Co and 0.1 to 0.7% for RE.

### 2.3. *MM-cobalt alloys*

In the light of this standardisation, a few MM-cobalt alloys (arc melted) were analysed for RE, Co and Fe (table 4). Co of purity 99.28% and MM (F) were used for arc melting. The pure Co value in A<sub>4</sub> and A<sub>5</sub> are respectively 55.67 and 56.04. The obtained values differ from these by -0.3% and +0.2% which are well within the tolerance. The sum total of RE and Fe obtained in A<sub>4</sub> and A<sub>5</sub> are respectively 43.23 and 42.81 as against the MM content 43.92 and 43.55. The differences are respectively -1.57% and -1.70%. The impurity levels in MM(F) as found

Table 3. Complexometric determination of Fe, Co and Total RE in synthetic mixtures.

Sample No.	Taken in mg			Found in mg (mean values)			% Error		
	Fe	Co	RE	Fe	Co	RE	Fe	Co	RE
D	..	175.86	95.00	..	175.57	94.80	..	0.2	0.2
E	5.98	122.72	70.13	5.96	122.77	70.08	0.3	0.04	0.1
F	20.14	109.73	70.13	20.10	109.27	69.60	0.2	0.4	0.7
G	50.08	79.41	70.13	49.99	79.50	69.84	0.2	0.1	0.4
H	149.70	44.76	105.00	149.12	44.55	104.40	0.4	0.5	0.6

Table 4. Complexometric determination of RE, Co and Fe in MM-Co alloys.

Alloy	Wt. percent expected			Wt. per cent obtained (Mean values)			
	MM (F)	Co	Pure Co	RE	Fe	(RE+Fe)	Co
A <sub>4</sub>	43.92	56.08	55.67	40.33	2.90	43.23	55.50
A <sub>5</sub>	43.55	56.45	56.04	39.98	2.83	42.81	56.12

from table 1 vary between 1.13% to 3.29%. Thus in A<sub>4</sub> and A<sub>5</sub> the sum of RE and Fe agrees well within the expected levels.

### 3. X-ray fluorescence method

#### 3.1. Preliminary study

Bertin (1970) has described various techniques of sample preparation for x-rf analysis. First we tried borax bead technique, but had to abandon it due to the low precision obtained, with xenon filled proportional counters as well as due to dilution effect. We adopted the powder technique in which undiluted RE oxide mixtures were pressed into pellets at a uniform pressure maintaining the same degree of packing density. Standards prepared from reagent grade RE oxides, after the removal of absorbed moisture and CO<sub>2</sub>, were found to expand slowly even in a desiccator and were not giving reproducible peak intensities. Synthetic mixture of oxides prepared from pure metals when analysed on the basis of the above standards gave only low peak intensities for Ce, La, Nd and Pr. Unlike the RE oxide pellets, the synthetic oxide pellets prepared from pure metals did not show appreciable expansion. These pellets gave reproducible peak intensities also. This was found to be due to different oxide powder characteristics. Therefore it was decided to use the same procedure for making the metal oxides for the standards and samples. In order to avoid absorption of moisture and to retain the same density throughout the measurement, the time interval between the removal of sample from the furnace and its analysis was kept at a minimum.

#### 3.2. Sample preparation

The composition of the standards used are shown in table 5. The metals were weighed, dissolved together in HNO<sub>3</sub> (1 + 1), evaporated to dryness and ignited at 900° C in a muffle furnace for 8–10 hr. in Pt crucibles. The oxides thus obtained were powdered well using a mortar and pestle and kept back in the furnace. To get the same packing densities, equal quantities (1 g) of the oxides from the standards and test samples were pressed into pellets of dia  $1.27 \times 10^{-2}$  m at a uniform pressure of  $4.340 \times 10^7$  kg/m<sup>2</sup> in a universal tensile testing machine operated in compression mode. The test samples were prepared by similar treatment. The samples used were taken from the same three different pieces of MM(F) and the one of MM (B) as used in the complexometric analysis.

## 3.3. Instrumentation and choice of spectral lines for analysis

General Electric XRD-6 Spectrometer with LiF (200) planes ( $2d = 4.028 \text{ \AA}$ ) and  $\text{SiO}_2$  (20 $\bar{2}$ 3) planes ( $2d = 2.75 \text{ \AA}$ ) analysing crystals,  $2.54 \times 10^{-4} \text{ m}$  detector slit and a xenon-filled proportional counter was employed for the x-rf analysis. Tungsten target x-ray tube operated at 60 kV and 50 mA was selected as the source of primary radiation. The LiF crystal was aligned by scanning the peaks of Zn and Cu from a brass piece at a scanning rate of 0.2 degrees per min. Suitability of the use of LiF and  $\text{SiO}_2$  crystals for the present analysis were evaluated using a standard pellet.

Following Lytle *et al* (1957) the analytical lines were chosen from the L-spectra as these are excited efficiently, see table 6 and also Gupta and Bhat (1974).  $L_1$  and  $L_2$  lines of Ce gave insufficient resolution when  $\text{SiO}_2$  crystal was used. So LiF crystal was used for the analysis of Ce, for which these two peaks superimpose. For La, LiF was used as the  $2\theta$  angle for La  $L_1$  and La  $L_2$  with  $\text{SiO}_2$  crystal is out of the  $2\theta$  range of the spectrometer.  $\text{SiO}_2$  crystal was used for Nd and Pr, because the resolution with LiF crystal was insufficient.

Table 5. Composition of standards for x-rf analysis.

Number	Oxide weight per cent			
	Ce	La	Nd	Pr
1	39.76	35.08	16.31	8.85
2	46.45	28.74	18.36	6.46
3	52.22	22.29	21.18	4.31
4	60.18	14.72	23.97	1.13

Table 6. Analytical spectral lines and  $2\theta$  angles used for Ce, La, Nd and Pr.

Element	Spectral line	Order	Relative Int. of L lines	$2\theta$ angle	
				LiF	$\text{SiO}_2$
Nd	$L\beta_1$	1	80	65.10	104.02
Pr	$L\beta_1$	1	80	68.23	110.48
Ce	$La_1$	1	100	78.99	137.39
Ce	$La_2$	1	10	79.33	138.45
La	$La_1$	1	100	82.88	151.61
La	$La_2$	1	10	83.23	153.22

## 3.4. Analysis, results and discussion

One standard at a time was removed from the furnace, made into a pellet and analysed immediately. To avoid possible moisture absorption during analysis, due to long exposure of pellets to atmosphere, a continuous tracing of fluorescent radiation peaks was preferred over the more accurate step scan technique. The fluorescent radiations dispersed by LiF or SiO<sub>2</sub> crystals were traced at a scanning rate of 0.2°/min in the appropriate  $2\theta$  angular regions to record the chosen L spectral lines of the rare earths. The peak intensities *versus* the weight per cent of the rare earth oxides were plotted. From the calibration curves shown in figure 1, it can be seen that the curves are linear and reasonably steep in the range studied. This linear relationship is due to the fact that the composition range of analysis is small.

The fluorescent radiation peaks for the test samples were also traced and the oxide contents in the test samples were obtained from the calibration curves. The

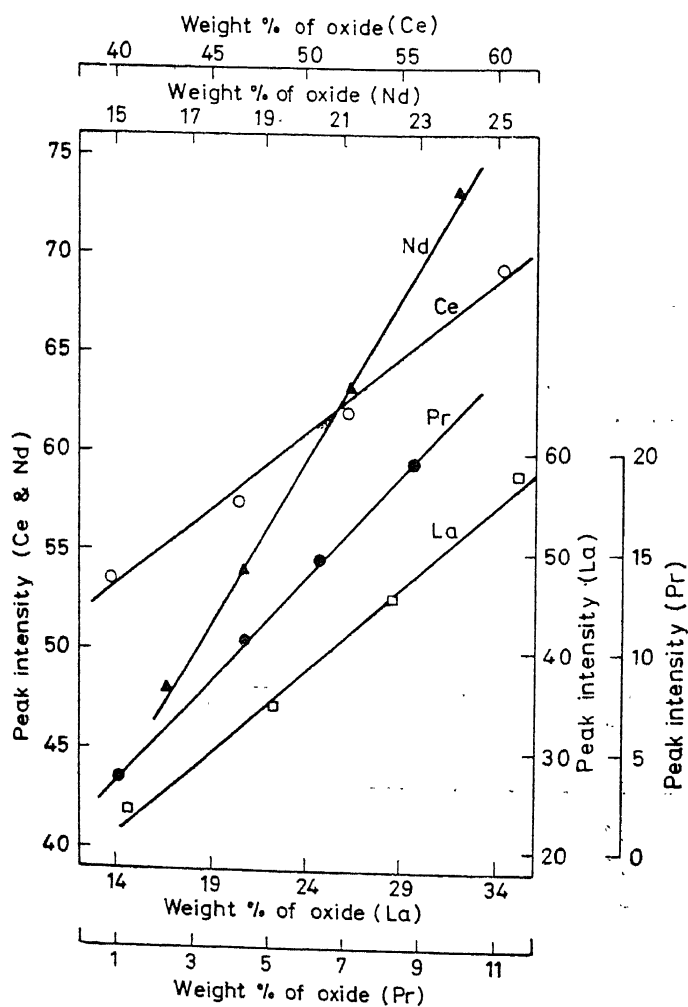


Figure 1. Calibration curves for Ce, La, Nd and Pr.



Table 7. X-rf analysis of mischmetals.

Sample	Weight per cent					Total	Mean
	Ce	La	Nd	Pr			
MM(F) 1	45.21	21.63	21.01	6.31		94.16	
MM(F) 2	44.33	22.21	21.63	5.96		94.13	
MM(F) 3	43.35	22.36	21.46	6.25		93.42	93.90
MM(B) 4	50.62	21.23	19.98	6.44		98.27	98.27

oxide contents obtained were converted to those of respective metals. Knowing the weights of MM taken and the weights of oxides obtained, the weights and percentages of the metals in the MM are calculated. The results are shown in table 7. We did not observe the spectral lines for Sm in MM, while scanning the peaks of various elements for qualitative x-rf analysis. On the basis of qualitative analysis of both the MM, we analysed only the four RE elements ; Ce, La, Nd and Pr.

It is usually reported that the accuracy of x-rf method of individual RE analysis is not very high and there could be an error of about 1% or more. The complexometric analysis of small pieces taken from various parts of a bigger piece in MM(F) shows reasonably large variations in the total RE content whereas the variation is not so high in MM(B). The difference in the values between the x-rf and complexometric methods could be due to the above reasons. MM(F) and MM(B) are produced from the same raw material. The present analysis however shows that MM(B) has a higher Ce content than MM(F).

#### 4. Conclusions

The position of the spectral lines for Fe and Co are far away from the spectral lines of the RE elements. This shows that Fe and Co do not have any influence in the measured intensity of the four REs. Therefore this method can be used for the determinations of individual RE in MM-Co and MM-Co-Fe alloys. The total RE, Fe and Co can be determined by complexometric method.

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