Recent Chinese Research on Analytical Chemistry of the Rare Earths

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The People's Republic of China has the world's largest reserves of rare earths. Recently, the rare earths have been found various applications in different fields of science and technology. The extensive research on analytical chemistry of rare earths has been made by Chinese analysts. The third Chinese Conference on the Analytical Chemistry of Rare Earths was held in 1982. A 2 volume treatise entitled "Analytical Chemistry of the Rare Earths" has been written by Cheng Jai-kai, Tseng Yung-ao, Luo Quing-yao et al. *[1]. The following is a short review of Chinese progress in analytical chemistry of the rare earths. Only developments of the past five years (1978–1983) will be described.*

Separation and Preconcentration

Precipitation and solvent extraction procedures are usually suitable for the separation of rare earths from other elements. Chromatography is used most often for the separation of the individual rare earth elements from each other.

The solubility of the hydroxide precipitates of rare earths is slight, but the selectivity is low. In order to increase the selectivity, suitable masking reagents are employed for the separation of micro amounts of rare earths, from other elements in large quantities. The rare earths can be separated from large amounts of Fe, Al, Ca, Mn and Cu using Mg as a carrier, and EGTA, TEA and H_2O_2 as masking reagents. This method has been applied to the analysis of ores [2, 3] and steels [4].

Various β-diketones are effective extractants for the rare earths. One of the more widely used is 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5 (PMBP). The use of PMBP as extractant may separate rare earths from large amounts of elements such as Ca, Mg, Al, Cr, Ni, Mn, Zn, Co, Cu, Ti, Fe, Nb, Th, Zr, V, Mo and W in solfosalicylic acid and NH_4CNS media. It is more frequently applied to the analysis of U, Th, Ca, steels, alloys and ores [5, 6]. The composition of the ternary complex RE–PMBP–TBP is $RE(PMBP)_3(TBP)_{2-3}$ [7].

We have already reported the separation of 5–1000 μg of rare earths from 500 mg of Fe(III), 80 mg of Ca, 50 mg of Mg, 30 mg of Ti, 20 mg of Zr, Sr, Nb, 10 mg of Mn, Al, 1 mg of Ba and 40 μg of Th, using HCl–tartaric acid as eluant on the cation exchange column [8]. This method can be used for the separation of micro amounts of rare earths in ores. Sm, Eu, Gd and Dy (0.02–0.05 ppm) can be separated and preconcentrated from 2–3 g of nuclear purity U [9], Al [10] and Zn [11] using HCl and H_2SO_4 as eluant on micro cation exchange column. A systematic chemical analysis of a yttrium-containing rock sample was carried out with use of a similar method [12].

The cation exchange separation and direct spectrophotometric determination of U(VI), Th, Zr, Sc and Ln using Arsenazo M [13] and p-acetylarsenazo [14] as eluants has also been proposed, along with the mechanism of various media effects.

Chen Cunzhi *et al.* [15] have designed and prepared a simple forced flow liquid chromatographic apparatus for the separation of trace amounts of rare earths, Y and Zr in alloy steels and high-temperature alloy steels.

The ion exchange chromatography is often applied to separate and preconcentrate trace amounts of the rare earth impurities in high-purity rare earths. α-Hydroxyisobutyric acid (α-HIBA) is an efficient eluant for the separation of rare earths. Cheng Jai-kai *et al.* [16] selected α-HIBA as an eluant to separate La, Ce, Pr, Nd, Sm and Eu from 1 g of high-purity yttrium oxide. The concentration factor is 10,000. Detailed studies on the parameters of separation (the characteristic of resin, column height, concentration and acidity of eluant) have been made. This method has been applied to routine analysis of high-purity yttrium oxides (Table I). A similar method has been used for the separation and pre-concentration of trace amounts of the rare earth impurities in almost all high purity rare earths except Ce and Eu [5]. Pan Yaohua *et al.* [17] proposed a simple and convenient method for estimating the concentration of α-HIBA in the separation of various high-purity rare earths.

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TABLE I. Separation and Preconcentration of Trace Rare Earth Impurities in High-Purity Rare Earth Oxides.

Sample	Sample taken (g)	Conc. factor	Stationary phase	Mobile phase	Detection limit** (ppm)	Recovery (%)	Ref.
Y_2O_3	1	10000	Porous resin ~200 mesh 2 X 60 cm	0.15 *M* α-HIBA pH 5.4 –Y 0.50 *M* α-HIBA pH 5.4 –La–Eu	0.008–0.03	91–96	16
Y_2O_3	0.25	10000	HEH(EHP)–silica gel* 1.6 X 30 cm	0.7 *M* HCl–La–Gd	0.25–0.38	92–105	22
Y_2O_3	1	20	Naphthenic acid–silica gel* 0.9 X 100 cm	0.4 *M* HCl–Y 2% HCl–alc. –La–Lu	0.013–0.5	83–118	26
Y_2O_3	0.25	8000	N 263–silica gel* 1.1 X 72 cm	2.0 *M* NH_4SCN–Y 0.1 *M* HCl–Tb–Lu	0.062–0.76	85–109	27
Nd_2O_3	1.5	38	HEH(EHP)–silica gel* 2 X 80 cm	0.12 *M* HCl–La–Pr 4 *M* HCl–Sm, Y	2.5–7.5	96–110	23
Sm_2O_3	0.4	200	Zerolit 225 200–400 mesh 1 X 20 cm	0.18 *M* α-HIBA pH 4.8 –Eu, Gd 3 *M* NH_4Ac–Pr,Nd	0.05–4.6	75–110	1
Gd_2O_3	0.1	500	Zerolit 225 150–200 mesh 2 X 25 cm	0.15 *M* α-HIBA pH 4.6 –Tb–Lu	0.05–1	85–115	35

*Porous silanised silica gel (100–200 mesh), 50 °C. **Emission spectroscopic method.

Cheng Jai-kai *et al.* [18] separated micro La in pure cerium and mixed rare earths by means of the ion exchange separation using α-HIBA as eluant on micro column (2 mm X 50 mm).

Zhao Guiwen *et al.* [19] separated 16 rare earth elements by high performance liquid chromatography using pH gradient elution with α-HIBA. Separation was completed in 75 min. More recently, 13 rare earth elements also were separated using pH and concentration simultaneous gradient elution with coulometric determination of Tm, Yb and Lu [20].

In recent years, extraction chromatrography has been used as an effective method for the separation and pre-concentration of trace amounts of the rare earth impurities in high-purity rare earths. In comparison of the acidic phosphorus-based extractants 2-ethylhexyl hydrogen-2-ethylhexylphosphonate, HEH(EHP) with HDEHP, Peng Chunlin *et al.* [21] found that the average separation factor for rare earths using both of the extractants are very approximate, $\beta = 2.5$. Since there is a C–P bond in the HEH(EHP) molecule, the acidity of HEH(EHP) is lower than that of HDEHP. The heavy rare earths are easily back-extracted, they may therefore be eluted separately with acids of lower concentration. The extraction chromatographic system HEH(EHP)–HCl has been applied to chemical spectroscopic analysis of high-purity Y_2O_3 [22] and Nd_2O_3 [23]. This system has also applied to the separation and spectrophotometric determination of La in ores [24]. Zhang Tao *et al.*, [25] observed the effect of loading capacity of rare earths on chromatographic peak in a HEH(EHP) extraction chromatographic system.

Peng Chunlin *et al.* [26] reported that trace amounts of 14 lanthanide impurities in high-purity yttrium oxide have been separated by extraction chromatography with naphthenic acid–hydrochloric acid system and determined by spectroscopy. Amine based extractants such as methyltrialkylammonium chloride (N 263) have been used as a stationary phase and NH_4SCN as an eluant for the separation of the heavy rare earth elements in high-purity yttrium oxide by extraction chromatography [27]. Pr and Nd have been separated by extraction chromatography and determined by spectrophotometry with N263-DTPA systems [28].

Thin layer chromatography is an excellent method for the separation of the individual rare earths. Cheng Jai-kai *et al.* [29] proposed a method for the separation of La, Ce, Pr, Nd and Sm by using silica gel and NH_4NO_3 as stationary phase, and tributyl phosphate, methyl ethyl ketone, ethyl acetate and HNO_3 (24:45:13.5:2.4) as developers. These rare earth elements were determined by spectrophotometry, with satisfactory results. This method has been applied to the separation and determination of La, Ce, Pr and Nd in monazite.

Methyl ketone NH_4SCN is a better developer for the separation of rare earths by paper chromatography. After improvement of the procedures, the separation of up to 4.7 mg of 15 rare earth elements has been carried out and the method has been employed to analyze ores [30].

Studies on reversed phase paper chromatography using HEH(EHP) as the stationary phase and HNO_3 as the mobile phase for the separation of lanthanide elements have been reported [31]. Liu Chiu-chun [32] has written a review about the separation of rare earths by gas chromatography.

The reports referred to the separation of rare earths by using inorganic ion exchangers are few. We have separated Th, Ln and U(VI) by chromatography on paper impregnated with ammonium molybdophosphate using a solution of HNO_2–alcohol as developer [33]. The trace amounts (0.2–5.0 μg) of rare earths can be separated from 1 g of high-purity compounds of uranium by eluting with a solution of HCl–NH_4Cl on the ion exchange column of zirconium tungstate and determined by spectrophotometry. Sr, Co, Ce (Eu) and Cs can be quantitatively separated from each other by eluting with a solution of HNO_3–$NaNO_3$ on the ion exchange column of thallium tungstate. More recently, the quantitative separation of Sc and Ln [34] on the ion exchange column of chromium arsenate has been studied.

Volumetric Methods

Chen Yongzhao *et al.* [36] used malic acid as a new masking reagent for masking the light rare earths in complexometric titration. The rare earths are complexed with EDTA (in excess), and the excess of EDTA is titrated with lead nitrate solution using xylenol orange as indicator at pH 5.6. After addition of malic acid, EDTA is displaced from the RE–EDTA complexes, then it is titrated spectrophotometrically with lead nitrate. More than 20 kinds of cations do not interfere with the determination of 50–500 μg of the light rare earths.

Mo Jinyuan [37] proposed coulometric complexometric titration of micro amounts of cerium. The Ce(III) is complexed with EDTA, and unused EDTA is titrated coulometrically with Hg(II) electrogenerated from mercury anode electrolysis. Malic acid is then added to form a complex with Ce(III) and to release EDTA, which is further titrated with Hg(II) using two polarized mercury-plated electrodes for endpoint detection.

Wang Houji *et al.* [38] prepared an alizarin-S ion selective electrode and used it as an indicator electrode in the potentiometric titration of Sc and rare earths with EDTA and alizarin-S at pH 3–3.5. The method is suitable for the determination of Sm in Co–Sm alloys.

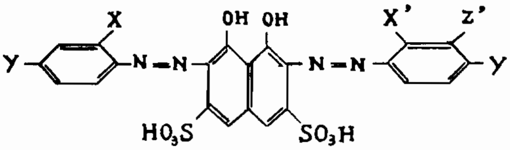
Li Lingying *et al.* [39] suggested a rapid complexometric titration method for determining the individual components of $LaNi_5$ and $SmCo_5$ alloys. An excess of EDTA is added and back titrated with lead acetate solution using xylenol orange as indicator. Sodium fluoride is added to displace EDTA from the RE–EDTA complex, then EDTA is titrated again with lead acetate to the end point.

The potentiometric titration of Ce(IV) employed an ion exchange diaphragm to substitute the salt bridge. The lower limit of the determination is 0.1 μg. This method was applied to determine Ce(IV) in silicate glass [40].

Spectrophotometry

Spectrophotometry is usually applied to determine micro amounts of the sum of the rare earths. Recently, because of the synthesis of new color reagents, the use of various complex reactions, the choice of suitable masking reagents and the study of color reactions of multi-component complexes, the sensitivity and selectivity for determination of rare earths has increased. The direct spectrophotometric determination of micro amounts of cerium earths, yttrium earths some individual rare earth elements and the sum of the rare earths without separation procedure can be achieved.

The symmetrical bisazo derivatives of chromotropic acid such as arsenazo III and chlorophosphonazo III are extremely useful color reagents, but the unsymmetrical bisazo derivatives of chromotropic acid appear to have better performances. Addition of various auxochrome groups to one side of the benzene ring which has no $-AsO_3H_2$ (or $-PO_3H_2$) led to a series of derivatives being synthesized, from which some high sensitive and selective color reagents of rare earths have been discovered. The following is the structure of these reagents:



(1) *p*-acetylarsenazo (Ar–*p*A): $X = -AsO_3H_2$; $Y' = -\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$
(2) *p*-bromoarsenazo (Ar–*p*B): $X = -AsO_3H_2$; $Y' = -Br$
(3) *m*-bromoarsenazo (Ar–*m*B): $X = -AsO_3H_2$; $Z' = -Br$
(4) *m*-acetylchlorophosphonazo (CPA–*m*A): $X = -PO_3H_2$; $Y = -Cl$; $Z' = -\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$
(5) *m*-formylchlorophosphonazo (CPA–*m*F): $X = -PO_3H_2$; $Y = -Cl$; $Z' = -CHO$
(6) *p*-formylchlorophosphonazo (CPA–*p*F): $X = -PO_3H_2$; $Y = -Cl$; $Y' = -CHO$
(7) *p*-iodochlorophosphonazo (CPA–*p*I): $X = -PO_3H_2$; $Y = -Cl$; $Y' = -I$
(8) *m*-nitrochlorophosphonazo (CPA–*m*N): $X = -PO_3H_2$; $Y = -Cl$; $Z' = -NO_2$

(9) *p*-nitrochlorophosphonazo (CPA–*p*N): X = $-PO_3H_2$; Y = $-Cl$; Y′ = $-NO_2$
(10) *m*-carboxychlorophosphonazo (CPA–*m*K): X = $-PO_3H_2$; Y = $-Cl$; Z′ = $-COOH$
(11) *m*-phosphonochlorophosphonazo (CPA–*m*P): X = $-PO_3H_2$; Y = $-Cl$; Z′ = $-PO_3H_2$

The color reactions of these reagents with rare earths and their applications are shown in Table II.

Yu Ximao *et al.* [41] have synthesized a series of unsymmetrical biarsenazo derivatives. The complex of p-bromoarsenazo [42] with cerium whose mol. absorbability is 3.53×10^5 l/mol·cm (713 nm), is the most sensitive reagent [43]. *p*-Acetylarsenazo has been applied to direct spectrophotometric determination of >0.001% Ce earths in alloy steels with satisfactory results [44]. Sensitivity is very high (670 nm, $\epsilon = 1.0 \times 10^5$) for the determination of Th in 1 N HCl [45].

Wu Bincai *et al.* [46] and Chen Zhenhua *et al.* [47] have synthesized a series of unsymmetrical biphosphonazo derivatives which can react with rare earths and which have high selectivity in strong acid ($pH < 1$). *m*-Acetylchlorophosphonazo [48–50] and *p*-iodochlorophosphonazo [51] were applied to determine the sum of the rare earths. *m*-Nitrochlorophosphonazo [52–54] and *m*-carboxylchlorophosphonazo [55] can determine cerium earths.

Chlorophosphonazo III forms β-type complexes with yttrium earths, while chlorophosphonazo III forms α-type complexes with cerium earths. By using the complex reactions of different type, yttrium earths and cerium earths can be determined. The cerium earths (α-type, 684 nm) and yttrium earths (β-type, 740 nm) at pH 3.0, and Y (β-type, 740 nm) at pH 1.8 can be determined. This method can be used for the determination of cerium earths, yttrium earths and Y in cast iron [56]. The reaction order of β-type complexes of yttrium earths with chlorophosphonazo III in buffer system (NaAc–HCl) and unbuffer system is 1 and 2 respectively. A reasonable mechanism has been suggested [57].

Cai Ruxiu *et al.* [58] have researched α-type and β-type color reactions of rare earths with some bisazo derivatives of chromotropic acid. Under certain conditions biphosphonazo reagents can react with yttrium earths to produce β-type complexes, and biarsenazo reagents can react with cerium earths to produce β-type complexes. In order to convert α-type complexes to β-type complexes an electrophilic group must add to *p*(*m*)-benzene ring of the azo group. For example, yttrium earths can be determined with *p*(*m*)-formylchlorophosphonazo in the presence of cerium earths [59], but *p*-acetylarsenazo can only react with cerium earths to form β-type complexes [60].

The studies on color reactions of multi-component complexes are quite active. The applications of multi-component complexes systems can increase the sensitivity and selectivity for the determination of rare earths. The micellar solubilization spectrophotometry in the presence of surfactant made great progress (Table III). Sc–chrome azurol-S–amphoteric surfactant system (dimethyldodecylammonioacetic acid, DDMAA) [61] and Sc–eriochrome azurol B–emulsifying agent (OP) system [62] are very sensitive ($\epsilon = 2–3 \times 10^5$). The quaternary complexes (RE–triphenylmethane dyes–organic alkali–surfactant), which not only have high selectivity of ternary mixed ligand complexes but also have high sensitivity of micellar solubilization systems, attracted our

TABLE II. Some New Color Reagents for Spectrophotometric Determination of Rare Earths.

Reagent	Determined element	Acidity	λ_{MR} (nm)	$\epsilon_{MR} \cdot 10^{-4}$	M:R	Application	Ref.
Ar–*p*A	La–Nd	pH 2.0–2.5	670	10.3–11.6	1:2	Steel, ore	44
Ar–*p*B	La–Nd	pH 4.7	713	26.2–35.3	1:2	Mixed RE	42, 43
Ar–*m*B	Ln–Y	pH 3.2–4.5	654–666	9.0–10.6	1:2	Soil, water, steel	83
CPA–*m*A	Ln–Y	pH 1	660	7.5–8.8	1:4	Steel, ore	48–50
CPA–*m*F	Ln–Y	0.1 N HCl	665–670	9.26–10.0			59
	Gd–Lu–Y	pH 3.0	696–698*	12.5–13.0		Mixed RE	59
CPA–*p*F	Ln–Y	0.1 N HCl	670–677	8.06–9.08			59
	Tb–Lu–Y	pH 3.5	728–731*	8.23–10.0		Mixed RE	59
CPA–*p*I	Ln–Y	0.2 N HCl	676–686	9.7–10.8	1:2	Soil	51
CPA–*m*N	La–Nd	pH 1.7	666	7.8–8.2	1:3	Castiron	52–54
CPA–*p*N	Y	0.1 N HCl	730*	6.67		La–Ce	84
	La–Ce	0.1 N HCl	674	7.09–7.14		Yttrium earths	84
CPA–*m*K	La–Ce	0.2 N H_2SO_4	660	8.1–8.6	1:3	Castiron, steel	55
CPA–*m*P	Ln–Y	0.1–0.2 N HCl	685–690	8.9–9.8			85
	Yb, Y	pH 3.4–4.0	745–775*	6.9			85

*β-type complexes.

TABLE III. The Color Reactions and Application of Multi-Component Complexes.

Determined element	Complex	MR	pH	λ (nm)	$\epsilon \cdot 10^{-5}$	Application	Ref.
Sc	Sc–CAS–DDMAA	1:2:4	7.0–7.8	620	3.0	Ore	61
Sc	Sc–ECAB–C_8NBr–NaC_8S	1:2	9.0	638	1.81		85
Sc	Sc–ECAB–OP	1:3	5.8–6.8	659	2.43		62
Ce	Ce–STA–CTMAB	1:3	6.8	580	0.61–0.84	La_2O_3, Ce earths	86
La–Lu–Y	RE–CPA–III–CTMAB	1:3:6	1.2 N HCl	705	0.42–0.47	Steel, Al	87
La–Nd	La–CPA–C–CPB	1:4	0.14 N HCl	692	1.9–2.1	Tb–Lu–Y	67
La–Nd	La–CPA–mF–CTMAB	1:4:8	0.1 N HCl	680	1.5–1.7	Alloy steel	88
La–Nd	Ce–Ar–J–CPB		1.5	710	3.44		68
La–Tb	Ce–Ar–G–CPB	1:1:2	1.3	699	1.60	Al–based alloy	89
Sc	Sc–CAS–CPB–Alcohol		5.5	615	2.31	La_2O_3, Gd_2O_3, Y_2O_3	90
Y earths	Yb–CAS–phen–CTMAB	1:2:1:4	8.4	631	0.97–1.36	RE_2O_3	91
Y earths	Y–CAS–phen–DDMAA	1:2:1:4	8.3	638	1.40	Ce earths	64
La, Gd	Lu–CAS–dipy–DPC	1:2:1:4	9.5–11.5	638	1.08–2.23	$(LaGd)_2O_2S$	92
Nd, Sm	Ho–ECR–dipy–CTMAB	1:2:1:6	9.7	610	1.60	Nd–Sm	65
Er, Gd	Nd–ECAB–n-phen–CTMAB	1:2:1:4	10.0	620–639	1.96	5 fold of La	93
Nd	Nd–Y–BPR	1:1:2	5.3	660	0.61	Y–Al garnet	72

attention. RE–eriochrome cyanine R–1,10 phenanthroline–CTMAB systems [63] and RE–chrome azurol S–1,10 phenanthroline–DDMAA systems [64] can be used to determine yttrium earths in mixed rare earths. RE–eriochrome cyanine R–α,α-dipyridine–CTMAB systems [65] can be employed to determine Sm in Nd–Sm mixture.

The micellar solubilization spectrophotometry, which frequently uses triphenylmethane dyes as color reagent, has high sensitivity but lower selectivity in neutral or alkaline media. Some new bisazo color reagents synthesized by Chen Zhenhua *et al.* [66] can form micellar solubilization complexes with rare earths in acid media (>0.1 N HCl). The systems of cerium earths-amino C acid chlorophosphonazo–CPB in 0.14 N HCl media can permit a majority of common metals (up to 40 mg) [67]. Cerium earths–amino J acid arsenazo–CPB systems at pH 1.5 produce very sensitive color reactions ($\epsilon = 3.44 \times 10^5$), which can be applied to the direct spectrophotometric determination of micro cerium earths in aluminium alloys [68]. Th–amino G acid chlorophosphonazo–TPC ternary complex for the spectrophotometric determination of Th appears to have very high sensitivity ($\epsilon = 1.7 \times 10^5$) [69]. In spectrophotometric analysis of rare earths a kind of co-coloration effect always appears, which interferes with the spectrophotometric determination of rare earths. Shen Hanxi *et al.* systematically researched co-color reactions of carboxynitrazo [70], chlorophosphonazo III [71] and bromopyrogallol red [72] with rare earths, and discovered that co-color reactions are due to formation of certain component mixed polynuclear complexes. (Table II).

Zeng Yune *et al.* [73] determined Sc and rare earths in RE–amino C acid chlorophosphonazo systems by means of dual (three) wave length spectrophotometry. He Xiwen [74] studied absorption spectra of mixed rare earths using linear programming to calculate the contents of the individual rare earths in mixed rare earths (La, Ce, Pr, Nd, Sm, Y, Yb). Lin Zhixin *et al.* [75] studied the effect of co-color reactions on the analysis of rare earths, using regression analysis of experiment results.

Primaquine and Ce(III) in 0.1 N H_2SO_4 produce bright red-violet colorations which have been applied to detect Ce(III), the limit of detection being 0.5 μg. Since rare earths and many ions do not all react with primaquine, it can be used to detect Ce(III) in mixed rare earths [76].

Cheng Jai-kai *et al.* [77, 78] studied the color reaction of water soluble α,β,γ,δ-tetra-(4-trimethylammoniumphenyl) porphine, T(4-TAP)P with Cu(II) and Zn(II). Large amounts of rare earths do not interfere with the determination. This method can be applied to spectrophotometric determination of ppb level of Cu [79, 80] and Zn [81] in high-purity rare earths without separation procedures.

Recently, because of the appearance of highly sensitive bisazo color reagents and the applications of masking reagents for eliminating interference, the reports containing the direct spectrophotometric determination of rare earths without separation procedure are extensive. Cheng Jai-kai *et al.* [82] have studied direct spectrophotometric determination of rare earths in ligand-buffer masking systems. Zn–EDTA, Zn–EDDD (ethylenediaminediaceticacid-diethyl acetate), Zn–HEDTA and Ca–C_yDTA were studied as ligand-buffer masking systems. The applications of ligand-buffer masking of metal chelates to the spectrophotometric determination of rare earths greatly increases the selectivity of masking, and the tolerance amounts of various interfering elements from μg to mg. The rare earths in cast iron, various steels and low alloy steels can be determined directly without separation procedures.

Zn–C_yDTA [56], Zn–EDTA [44] are usually used for masking the interference of yttrium earths in the spectrophotometric determination of cerium earths; NaF [56, 64] and $NaHCO_3$ [63] are usually used for marking the interference of cerium earths in the spectrophotometric determination of yttrium earths.

Oxalic acid [48, 52] is usually employed to mask the interference of large amounts of Fe(III), Al(III) *etc.* in the spectrophotometric determination of rare earths with phosphonazo color reagents at $pH > 1$.

Spectrophotofluorimetric Methods

Ci Yunxiang *et al.* studied the fluorimetric method of the acetylacetone complex of terbium [94] and the dipcolinic acid complex of terbium [95]. The lower limit for the determination of terbium is 4 ng/ml. This method was applied to determine micro amounts of Tb in rare earth oxides and LaOBr. Shi Hueiming *et al.* [96] have researched the fluorescent reaction of La, Y with oxine–5-sulforic acid in the presence of cationic surfactants. In comparison with their binary complexes, the fluorescence intensity of the ternary complexes increases by 4-fold and 10-fold. Y (2ppb) and La (20ppb) in the solution can be determined. La and Y in rare earth oxides have been determined. The sensitivity of Eu–TTA–diphenyl guanidine–acetone system is higher than the corresponding method of extraction in the absence of acetone. It can be applied to determine micro amounts of Eu in rare earth oxides [97].

Atomic Absorption Spectrometry

In comparison with the method using graphite tubes for atomic absorption spectrometric determination of rare earths, the sensitivity of the method using pyrolytic graphite tube increases 10-fold, and the reproducibility is much better [98]. Ma Yizai *et al.* [99] have determined U and rare earth elements by atomic absorption using a pyrolytic graphite tube lined with both tungsten and tantalum. The method gives 2 to 24 times better sensitivity in comparison with use of a conventional pyrolytic graphite tube; there is no memory effect. Eu, Nd, Sc and Ce in soil were determined; and the detection limits were 0.2, 20, 0.2 and 100 ppm, respectively. The results correlated well with those by neutron activation analysis. Chen Youwei *et al.* [100] determined 15 rare earth elements in ores by atomic absorption using a graphite oven. Hsiu Wensui [101] proposed tantalum-boat flameless atomic-absorption method for the determination of ytterbium in rocks.

Eu in rare earths of Baotou ores [102], Er and Ho in yttrium earth oxides [103] and Y in Ni base alloy [104] have been determined by nitrous oxide–acetylene flame atomic absorption spectrometry.

Emission Spectroscopy

Emission spectroscopy is a good method for the determination of micro amounts of rare earths. It is applied to determine micro amounts of rare earths in U, Ca, Al, Zn, pure rare earths and ores. The analysis of the individual rare earths used Ar–O_2 controlled atmospheres for eliminating interfering cyanogen bands, suppressing background and increasing sensitivity and precision of the analytical method. A D.C. are (14–15 A) is used as an excitation source combined within 2–3.4 M grating plane spectrograph and graphite powder as spectral buffer. The sensitivity of the analysis of some high-purity individual rare earths is shown in Table IV.

Jiang Zucheng *et al.* [105] observed the distillation phenomenon between light and heavy rare earths when a full use of the chloridized reaction in the electrode was carried out. The spectral buffer was made from cesium chloride, polyvinyl chloride and carbon powder. The controlled atmospheres carrier-distillation method was used for the determination of trace amounts of light rare earth impurities in high-purity yttrium oxide.

In order to increase the sensitivity of spectroscopic determinations, ion exchange chromatography, extraction chromatography, extraction and co-precipitation are usually employed for separation and preconcentration. The method has been applied to the determination of trace amounts of rare earths in nuclear materials, rocks, ores and high-purity rare earths (Table I).

In more recent years, attention has been directed to ICP spectroscopy, because of the small effect of matrix and low detection limits. This method has been applied to determine trace amounts of 14 rare

TABLE IV. Quantitative Determination Limits for Rare Earth Impurities in High-purity Individual Rare Earths by Controlled Atmosphere Emission Spectroscopy (ppm)*.

Matrix	Determined element															ΣRE	Ref.
	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y		
La_2O_3		10	10	5	5	1	10	10	1	1	1	1	0.1	10	3	68.1	110
Eu_2O_3	5	20	20	10	5		7	10	5	5	5	3	0.1	3	1	99.1	111
Gd_2O_3	5	10	10	10	5	2		20	5	10	5	3	0.5	10	3	98.5	112
Er_2O_3	5	30	50	10	30	5	50	50	5	6		17	5	50	3	316	113
Yb_2O_3	2.1	30	30	10	10	2	2	5	3	5	2	5		10	3	119.1	114
Y_2O_3	1	10	10	3	1	0.5	3	10	0.5	3	1	0.5	0.1	10		53.6	112
$(YEu)_2O_2S$	1	8	10	1	5		5	8	1	3	5	1	0.3	1		49.3	112

*PGS-2,2 M grating plane spectrography, 3.7 Å/mm.

earth elements in high-purity yttrium oxide. The detection limits of quantitative determination for most rare earth elements are 0.3–3.0 ppm except Ce and Pr. The relative standard deviation is 2.3–7.3% [106]. Huang Benli *et al.* [107] improved the ICP excitation source and studied the influence of some parameters on the ICP characteristics. The detection limits of Eu, Y, Yb are 0.0015, 0.0070, 0.0015 μg/ml respectively.

Hu Wenfan [108] proposed the application of ICP-atomic emission spectroscopy with direct powder introduction technique to simultaneous spectroscopic determinations of 32 elements in silicate samples. The measuring range is La, Sc 1–1000 ppm, Y, Yb 0.1–1000 ppm, respectively. The method is characterized by rapidity in analysis, higher sensitivity, better reproducibility, less memory effect and wide measuring range. Ge Weibao *et al.* [109] have used this method to determine the detection limits for 67 elements (containing 16 rare earth elements).

Polarographic Methods

Kao Sheaushya [115] reviewed investigations on polarographic analysis of rare earths. Yao Xiuren *et al.* [116] proposed that there is a polarographic catalytic wave at 1.5 V (*vs.* S.C.E.) in Sc–NH_4Cl–cupferron–diphenylguanidine system, the sensitivity is 1×10^{-7} *M*. Trace amounts of Sc in ores were determined by this method. The study of the mechanism showed that the wave is an adsorptive-complex wave [117], the composition of the adsorptive complex Sc:Cl:Cup:DPG is determined to be 1:2:1:1 with the conditional stability constant $\beta = 1.22 \times 10^{-7}$.

Yang Jinqin *et al.* [118] suggested that a sensitive polarographic catalytic wave appears at −1.45 V (*vs.* S.C.E.) in Yb–NH_4Cl–KNO_3 (or $NaNO_3$) system. The determination limit is 5.0×10^{-7} *M*. The method has been used to determine micro amounts of Yb in ores. After improvement of the method, Yb can be detected to 5×10^{-8} *M* [119]. The mechanism of this system has been investigated [120].

Kao Sheaushya *et al.* [121] proposed Eu–DTPA–NaCl system, the limit of detection of Eu(III) is 2×10^{-7} *M*. Small amounts of Eu in rare earth oxides have been determined by this method.

Yang Jinqin *et al.* [122] discovered that Y exhibits a polarographic catalytic wave in Y–rhodamine B–NH_4Cl system. Kao Sheaushya *et al.* [123] studied Y–rhodamine B–diphenylguanidine system. There is a linear relationship between the concentration of 1×10^{-7}–1×10^{-6} *M* Y(III) and the decreases of wave heights. The mechanism of this system has been researched, and results indicated that Y(III) may form an ion-association complex with rhodamine B and diphenylguanidine. The complex adsorbs strongly and occupies the partial surface area of the mercury drop, thus the wave height of rhodamine B itself decreases correspondingly.

There is a linear relationship between the concentration of 3×10^{-7}–2×10^{-6} *M* Sm(III) and the decreases of wave heights [124] in Sm–rhodamine B–diphenylguanidine system.

Kao Sheaushya *et al.* [125] presented an adsorption complex wave of La–oxine–maleic acid in KCl solution. The complex has the composition of La:OX:A = 1:3:1. The concentration of La(III) in the range from 5×10^{-7} to 5×10^{-6} *M* is proportional to the decreases of the wave heights, which has been used for the determination of La in the rare earths phosphor$(LaGd)_2O_2S$. The polarographic adsorptive complex wave of Tb–oxine–$NaClO_4$ also has been studied [126].

Dong Shaojun *et al.* [127] researched polarography of complexes of rare earths with murexide. The wave height is directly proportional to the concentration of rare earths within the range of 0.1–0.75 m*M*. It is thus possible to determine the individual or mixed rare earths.

Miscellaneous Methods

X-ray fluorescence spectrometry is a widely used analytical technique for the rare earths. This technique has been used for the determination of rare earths in minerals [128, 129], rare earth concentrates [130, 131], and magnetic materials [132, 133].

Spark source mass spectrometry is used for the determination of 0.1 ppm levels of rare earth impurities in high-purity yttrium oxides [134, 135]. Wang Zishu *et al.* [136, 137] reported that the trace amounts of rare earths in the mantle and moon rocks have been determined.

Neutron activation analysis offers a highly sensitive technique for the quantitative determination of rare earths. The rare earths in meteorites, rocks, soils, river waters, biologies, high-purity silicons [138] and environmental samples [139] have been determined.

Laser intra-cavity absorption spectrometry of Nd has been researched [140]. This method can be used for the determination of Nd in cerium earths.

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