ANALYTICAL
CHEMISTRY
OF THE
RARE EARTHS

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PREFACE

THE custom once was for a modest author to preface his work with an apologia for weighting his readers down with another intellectual tome aimed at filling a 'felt want'. The present author would present a slight variant on this theme. Having worked in the rare earth field for many years, and having done his fair share of testing and rejecting methods of analysis, he was aware of the need for a monograph attempting to rationalize and stabilize analytical techniques as applied to the rare earths. The apology, therefore, is not for the work presented, but for the author's temerity in undertaking such a presentation when several other workers could undoubtedly have done a better job.

Generally, information on techniques of rare earth analysis is widespread — like the rare earths. But again, like the rare earths, this information occurs only sporadically in useful quantities. Schoeller and Powell, Meyer and Hauser, Hildebrand and Lundell, Scott, and the writer's *Chemistry of the Lanthanons* (now grossly archaic) all provide guideposts to procedures. The more definitive work is, however, too often tucked away like old theatre programmes, and requires overmuch effort and too much perusal and study of the literature before the bench bound analyst can undertake the task of analysing a sample sent in three weeks ago for 'determination and specification of rare earth content'. I have tried to collect and construe these data in one modest volume.

I have no doubt that the many laboratories now working with the rare earths will have developed specific techniques for specific analyses and may decry the absence of these techniques from this monograph. At this moment, however, I feel the requirement to be for a work covering the general field of rare earth analysis. Nevertheless, the hope resides that readers who have developed specific techniques will communicate them for possible inclusion in any subsequent editions.

My appreciation goes to Prof. Louis Gordon who suggested and convinced me that I should prepare this monograph — I would have

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preferred it to emanate from his more able pen. I have been greatly aided moreover by encouragement, suggestions and recommendations from many of my past and present co-workers in this field, and most notably by my mentor, Dr J. K. Marsh of Oxford. To these and other chemists whose work, published and unpublished, has been a source of information — my deep appreciation. To my wife who typed the manuscript, and Pergamon Press who published it, my gratitude for having rendered legible my illegible scrawl.

But a final word of concern. Terminology has developed from an awkward word in a spelling bee to an International Conference on Nomenclature and, to avoid overmuch criticism from the pedantic semanticists, we must define our terms. Those used in this monograph, apart from the marginal comments, asterisks and calculations which undoubtedly and subsequently will appear, are those I suggested in *Chemistry and Industry* (London), June 26th, 1954. These may be conveniently summarized:

La+Ce+Pr+Nd+Pm+Sm+Eu+Gd+Tb+Dy+Ho+Er+Tm +Yb+Lu = lanthanons.
lanthanons+Y+Sc = Rare Earths.

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CHAPTER I

HISTORICAL INTRODUCTION

THE FIRST rare earth to be discovered — yttrium — was isolated from gadolinite in 1794[1]. One hundred and fifty years had to pass, however, before all members of the rare earth series had been separated and identified as entities. In retrospect, and knowing a little more about these elements, we may well be astonished that the early workers — Gadolin, Ekeberg, Mosander, Brauner, Urbain, von Welsbach, etc. — made such progress. Separation by prolonged and tedious processes of fractional crystallization, precipitation, etc., could be supplemented only by the crudest methods of detection and determination of individual rare earths. Confusion of description, terminology and even of individuality readily occurred because of this lack of analytic technique and instrumentation.

The earliest rare earth determinations involved, of course, identification via oxide or solution colour and equivalent weight. It was early realized that the rare earths could be precipitated almost *in toto* by oxalic acid from dilute mineral acid solution and that the insolubility of rare earth hydroxides would cause them to be found together with aluminium and iron in the third analytical group. Beyond this, the gravimetric techniques were essentially refinements of grosser scale separations, the usual analysis simply effecting separation of 'cerium' earths from 'yttrium' earths by precipitation of the double alkali sulphates[2], under more or less standardized conditions.

'Redox' titrations of cerium were soon discovered and applied[3] but this was apparently the early limit of individual determination. Curie's magnetic balance aided somewhat in following separation of elements, but so also did the simple equivalent, or average atomic, weight determination.

The difficulties of identifying individual rare earths were somewhat lessened when Gladstone first observed their absorption spectra in solution[4], but, paradoxically, this new application of spectroscopy was more of a hindrance than a help in rare earth chemistry. The

multiplicity of, for example, the neodymium and praseodymium absorption spectra led to many arguments about the individuality of the elements, there arising, rather transitorily, the school which claimed 'one absorption band — one element[1]'.

Apart from the early polynomial characterization of the rare earths, discrepancies and confusion arose because the early analysts too frequently were unaware of the valence state in which the element determined existed in the original material. Analyses for cerium, praseodymium and terbium, such as they were, were reported as the sesquioxides instead of the CeO_2, Pr_6O_{11}, Tb_4O_7, which had actually been determined. Despite the spectroscope and the magnetic balance, methods of purity determination were poor. A reasonably white product, resulting from fractional ammonia precipitation of a light lanthanon fraction, was totally considered to be lanthanum oxide with complete disregard for the $0.5-1$ per cent of ceria which it probably contained. Even with cerium itself, authoritative statements of the colour of the oxide varied from 'pure white' through 'salmon pink' to 'tan'. It is now appreciated that the oxide colour is somewhat dependent upon its mode of preparation and particle size[5]. In gravimetry, colour of the oxide was the prime criterion and, in volumetric work the purity, or rather impurity, level of the standard was determinative.

In many instances, of course, errors cancelled out and it becomes a source of continued surprise, not that the earlier workers obtained any results at all, but that all too frequently the results of earlier mineral analyses are within one or two per cent of figures which we now smugly assume to have been rectified and developed to the nth degree of modern techniques. Apart from determinations of the purity of the separated products, much of the early analytical endeavour in rare earth studies emanated from attempts to understand the geochemistry of their mineral occurrences. Many of the previously believed correlations of rare earth contents with associated elements we now know to be immature and grossly incorrect. Since, in general, mineral association is largely dependent upon similarities in cation size, co-ordination number and ionization potential[6] the most interesting and general associations of the rare earths are those involving titanium, the earth acids, uranium, and thorium. But it is separation from just these elements which produces the greatest inaccuracies in analyses as practised by the earlier chemists. An

interesting, if somewhat patronizing, exercise lies in the comparison of correlations given by Spencer[7], Meyer and Hauser[8] and Mellor[9] with the more recent studies of Vainshtein et al.[10], Ringwood[11], Murata et al.[12], Wylie[13] and Masuda[14]. But this is hardly germane to the present work and would serve essentially further to confirm the deductions of Goldschmidt and his co-workers[15] and of Rankama and Sahama[16]. Appendix I summarizes what may be considered authenticated geochemical associations of the rare earths.

In many instances errors crept into older analyses because of the lack of appreciation of the naturalistic chemistry of the rare earths. We understand now, how Bergman[17], d'Elhuyar[18] and Scheele[1] missed the honour of the first discovery of the rare earths in Crondstedt's and Hisinger's minerals by mistaking them for lime. It is similarly easy to understand even those modern analyses which have failed to account adequately for scandium through non-appreciation of its amphoteric nature[19].

As the uniqueness of rare earth absorption spectra became more appreciated and instrumentation improved, spectrophotometry was increasingly employed but errors were still encountered. The effects of anions and cations upon optical densities, extinction coefficients, and positions of the absorption bands were barely appreciated; some of the photographic techniques employed were only slightly more accurate than visual comparison of band intensities and of course the standards employed were frequently of dubious purity.

Analyses have not been consistently questionable, however. Between the two (so far) World Wars, our knowledge of the rare earths, and techniques for their analysis was extensively developed through the work of McCoy, James, Prandtl, Rolla, Marsh, Rodden, etc. But whenever gravimetric results were required (and this was frequently the case) or difference figures were inadmissible, recourse had to be made to the tedious fractional precipitation or crystallization procedures. Fraction checks of magnetic susceptibility, average atomic weight, or spectral absorption all played their part in determination of such elements as lanthanum, yttrium, gadolinium, etc., before results even slightly worthy of consideration could be obtained.

During this period analysis by emission spectrography underwent a major metamorphosis but only in the more recent years did standard rare earth materials of sufficient purity become available from which their emission spectra could be defined and tabulated correctly.

Even with this knowledge, the multifarious interferences occurring in the arc and spark still require much study and interpretation before satisfactory procedures can be established. The limitations and accuracy of these procedures will be dealt with subsequently.

The advent of the ion exchange era, propagated in England by Adams and Holmes[20] and nurtured through gestation, infancy and adolescence by workers on the Manhattan project[21] abruptly changed the conditions under which workers in the rare earth field existed. Although now applied on industrial scales, the earliest ion exchange processes and techniques could have been considered almost exclusively analytical tools. Many modifications and improvements have been developed over the past fifteen years and, in a later chapter, we shall consider only the most refined applications of ion exchange to the analytical chemistry of rare earths.

In large scale separational processes, solvent extraction techniques are competing with ion exchange on a widening basis; analytically however, solvent extraction has been employed for many years in many ways. Nevertheless, in rare earth analysis our present knowledge somewhat seems to limit the application of this procedure.

Probably the most recently developed instrumental technique applicable to rare earth analysis has been that of X-ray spectrometry. Whilst emission spectrography still appears to present the final criterion for detection and determination of small amounts (p.p.m.) of rare earths, X-ray studies appear to be becoming increasingly applicable and applied to analysis for larger quantities by reason of their rapidity, versatility and accuracy in comparison with spectrophotometry.

REFERENCES

1. VICKERY, *Chemistry of the Lanthanons*, Butterworths, London, 1953; *Chemistry of Yttrium and Scandium*, Pergamon Press, London and New York, 1959.
2. URBAIN, *Ann. Chim.*, *19*, 184 (1900).
   JAMES, *J. Amer. Chem. Soc.*, *34*, 757 (1912).
3. KNORRE, *Z. angew. Chem.*, *10*, 685, 717 (1897).
4. *J. Chem. Soc.*, *10*, 219, 1858; *11*, 36 (1859).
5. VICKERY, *Nature, Lond.*, *160*, 830 (1947).
   HARWOOD, ibid. *164*, 787 (1949).
6. ANDERSON, *Proc. Roy. Soc., N.S.W.*, 76, 329 (1943).
   AHRENS, *Geochim. et. Cosmochim. Acta*, *2*, 155 (1952); *3*, 1 (1953).
7. *Metals of the Rare Earths*, Longmans Green, London, 1919.

8. *Die Chemische Analyse*: *Die Analyse der Seltenen Erden und Erdsäuren*, Enke, Stuttgart, 1912.
9. *Comprehensive Treatise on Inorganic and Physical Chemistry*, London, 1929.
10. *Dokl. Akad. Nauk. USSR, 104*, 268 (1955); *Geokhimiya, 1958*, 245.
11. *Geochim. et Cosmochim. Acta, 7*, 189 (1955).
12. ibid. *4*, 292 (1953).
13. *Amer. Mineral., 39*, 667 (1954).
14. *J. Earth Sci. Univ. Nagaya, 5*, 125 (1957).
15. *J. Chem. Soc., 1937*, 655.
16. *Geochemistry*, Chicago, 1950.
17. *Opusc. Phys. Chem. Lipsiae, 6*, 108 (1780).
18. *Svenska. Akad. Handl., 5*, 121 (1784).
19. VICKERY, *J. Chem. Soc., 1955*, 251; *1956*, 3113.
20. *J. Soc. Chem. Ind., 54*, 1-6T (1935).
21. *J. Amer. Chem. Soc., 69*, 2769 (1947).

CHAPTER II

SAMPLE DECOMPOSITION

IN GENERAL, modes of attack of rare earth minerals and materials follow, on a more refined scale, those employed for decomposition of the mineral or ore before mass separation of the elements[1]. Many coarse procedures which are, however, applied on a massive scale — such as chlorination — have not thus far been adapted, and do not seem easily adaptable, to analytical techniques.

Early studies of rare earth chemistry rapidly showed that no one method of sample decomposition could be employed satisfactorily upon all types of rare earth materials. In this respect the analyst ultimately will have to exercise his own judgment as to the most suitable acid or reagent according to the nature of the determination required. Since metathesis of rare earth compounds to hydroxide is readily accomplished by concentrated sodium hydroxide solution, and the hydroxides are readily soluble in acids, only very infrequently will it be found that the rare earths cannot be obtained in solutions of acid most appropriate to subsequent determinations. As will be indicated later, however, the use of strongly alkaline solutions must be undertaken with particular care when scandium is, or is believed to be, present.

Fine comminution of samples is, of course, a prerequisite, and no analyst should consider decomposition of a sample until it has been reduced in an agate mortar to a particle size of at least 200 mesh. Even when thus finely divided some material will resist attack; particularly is this so with some samarskites and other materials containing the earth acids. These should therefore preferably be ground to —325 mesh before cautiously attacking with hydrofluoric acid.

Table 2-1 indicates reagents most appropriate for decomposition of the commoner minerals and compounds of the rare earths, and, for ease of reference, consideration and application of the major decomposing reactants are now treated *seriatim*.

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TABLE 2-1. REAGENTS FOR ORE DECOMPOSITION

H₂SO₄ and/or KHSO₄	HCl (with or without H₂O₂)	HF (or H₂SO₄+NaF)
Monazite	Allanite	Samarskite
Cerite	Gadolinite	Euxenite
Xenotime	Thorite	Fergusonite
Yttrotitanite	Wiikite	Yttrotantalite
Thorianite	Cerite	Thortveitite
Wiikite	Orthite	Polycrase
Yttrocerite	Bastnaesite	Davidite
Davidite	Lanthanite	Bazzite
Bastnaesite	Carbonates	Pyrochlore
Bazzite	Oxalates	Aeschynite
Carbonates	All oxides except Ce.	Yttrocrasite
Fluorides	Hydroxides	Risorite
Oxalates	Heliandite	
Oxides	Yttrotitanite	
Hydroxides	Kielhauite	
Samarskite	Yttrocerite	
Plumboniobite		
Risorite		

SULPHURIC ACID

The use of sulphuric acid for the 'cracking' of minerals has come down to us through the ages, and indeed some separational processes have been based upon its use. Because of the negative heats of solution and relatively low solubilities exhibited by the rare earth sulphates[1, 2] however, it would seem preferable to retain the rare earths in association with some anion other than sulphate. This is usually effected by following the initial acid attack by a hydroxide metathesis and then redissolving the obtained hydroxides in e.g. hydrochloric or nitric acids.

Sulphuric acid (or alkali bisulphate — see below) is generally employed in working up cerite, monazite, xenotime, etc., the finely ground ore being heated to decomposition with twice its weight of acid. Actually only about a quarter of this weight of acid is really necessary, but the excess maintains the mass fluid enough to allow reaction to proceed as the sulphates crystallize from the heated mass. On attack of monazite or other ceriferous ores by sulphuric acid, the mass gradually develops an orange-red colour owing to the formation of ceric sulphate $Ce(SO_4)_2$ or the acid

sulphate $CeH(SO_4)$. Overheating causes reduction and dehydration to the white tervalent sulphate $Ce_2(SO_4)_3$; it should be avoided unless subsequent metathesis is intended. Solubilities of some octahydrated rare earth sulphates are shown in Table 2-2. Scandium solutions

TABLE 2-2. SOLUBILITIES OF OCTAHYDRATED SULPHATES (g/100 g H_2O)

	20°C	40°C
La	3·80	1·50
Ce	23·80	10·30
Pr	12·74	7·64
Nd	7·00	4·51
Sm	2·67	1·99
Eu	2·56	1·93
Gd	2·89	2·19
Tb	3·56	2·51
Dy	5·07	3·34
Ho	8·18	4·52
Er	16·00	6·53
Yb	34·78	22·90
Lu	47·27	16·93
Y	9·76	4·90
Sc	28·50	33·60

excepted, aqueous solutions of these sulphates, made in ice cold water, deposit crystals of one or more hydrates $RE_2(SO_4)_3$ nH_2O with increase in temperature. The normal solubility of scandium sulphate in comparison with the inverse solubility of the other rare earths with temperature is an interesting phenomenon[3]. From the data given, the recommendations of earlier workers that ice cold water be employed for sulphate dissolution can be well appreciated. This lack of solubility of the sulphates is a great disadvantage in the use of sulphuric acid for mineral decomposition — that is, unless very high acidities or dilution be employed. In determining cerium by redox titration it is necessary that high acidities and concentrations be maintained, else hydrolysis of the Ce^{4+} ion occurs, with consequent precipitation of ceric hydroxide and basic sulphate.

After attack by sulphuric acid, concomitant lead, barium, calcium, silica, etc., remain as residue, and the analyst must be careful to ensure that no rare earth sulphate is occluded or entrained with them. As a matter of general precaution it is probably advisable to consider

sulphuric acid (or alkali bisulphate for that matter) as merely a primary means of decomposition. Once mineral breakdown is effected, the sulphate, dissolved or not, should be converted to hydroxide. Sodium hydroxide pellets or concentrated solution may be added directly but cautiously to the diluted sulphate slurry. If solid caustic alkali be used, heats of hydration and reaction are usually quite sufficient to raise the temperature of the mass to boiling point, and metathesis is accomplished almost instantaneously. The resultant hydroxides of the rare earths, iron, calcium, etc., are thus obtained in a heavy, readily filterable condition. The characteristic colour changes which occur during this treatment are due to the formation first of cerous, then ceroso-ceric, and finally ceric hydroxides. After washing twice by decantation, with hot distilled water, filtration and further washing, the hydroxides can be redissolved in nitric, hydrochloric or perchloric acids, reprecipitated by ammonium hydroxide, and filtered free from all but the last traces of phosphate, sulphate, etc.

Titanium, tantalum, niobium, hafnium and zirconium divide between the mineral acid solution of the hydroxides and the various filtrates but are removed from the dilute acid solution of the hydroxides by boiling. There is rarely need to adjust the pH of the acid solution of the hydroxides, since the amount of acid required for redissolution is very nearly theoretical and the pH of the solution seldom drops below 3·5–4 0. At this acidity level titanium, tantalum, niobium, etc., readily hydrolyse. In the finest work, however, the hydrolysed precipitate should be reworked for any rare earths which possibly may have been occluded. The precipitate should be filtered through a pad of paper pulp, the filter and precipitate digested with hydrochloric acid, and the solution thus obtained diluted to about 5 per cent acidity. After boiling to ensure reprecipitation of the earth acids, etc., the solution is again filtered, when any occluded rare earths will pass through into the filtrate.

If the initial attack by sulphuric acid be taken to dehydration of the sulphates formed, silica present will also be dehydrated and remain unaffected upon caustic metathesis, thus appearing finally with the rare earth hydroxides. Hydrolysis of the final acid solution for elimination of titanium, etc., will remove some silica, but where no hydrolysable elements are present the final acid solution should be evaporated to dryness, baked, redissolved in a dilute acid, and filtered

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free from the silica. Any silica entering the caustic solution and required for complete analysis may be recovered therefrom by normal means.

Procedure: Weigh 2 g of finely powdered monazite, xenotime, etc., into a 500 ml Phillips beaker. Moisten slightly with a few drops of water to avoid adherence of the ore to the beaker. Add 10 ml concentrated sulphuric acid, cover, and heat to SO_3 fumes until decomposition is complete (2–3 hr). Cool, first in air, then in an ice bath, and cautiously dilute with 100 ml distilled water. Stir gently to suspend the basic sulphate crystals and add cautiously 20 per cent sodium hydroxide solution or small sodium hydroxide pellets until the solution is alkaline (pH ca. 10). Boil for 10 min, then dilute to 400 ml with hot water. Allow to stand and wash the precipitated hydroxides three times by decantation with hot water. Finally, filter through a Whatman 541 paper and again wash twice with hot water. Return the precipitate to the original beaker and dissolve in the minimum of nitric acid, dilute to 50 ml, warm, and filter from unattacked zircon, rutile, etc.

BISULPHATE FUSION

Potassium bisulphate is usually recommended instead of the sodium salt for decomposition of rare earth minerals by bisulphate fusion. Not only are the minerals decomposed by this treatment, but double alkali sulphates are also formed and the sodium rare earth sulphates are, in general, less soluble than those of the potassium salt[4]. In practice, however, since subsequent hydroxide metathesis is again the preferred procedure, it would seem immaterial which alkali bisulphate be employed for the initial decomposition. Use of the potassium salt requires, however, a smaller excess of reagent than does the sodium salt, and far less reagent is generally required for bisulphate decomposition than in the sulphuric acid attack. An additional advantage of the fusion approach is, of course, the minimal amount of acid present in the final aqueous solution. The solid bisulphate cake obtained after mineral decomposition should be thoroughly disintegrated by boiling in water and aided by occasional light pressure from a glass stirring rod; the slurry obtained should be cooled somewhat before addition of solid sodium hydroxide. As has been indicated above, the colour change upon metathesis is interesting and clearly discernible when reasonable amounts of cerium are present. From the white-yellow sulphatic material the mass passes through grey, then purple phases indicating partial oxidation of the

cerium hydroxide produced. Under some circumstances, and particularly if the slurry be continuously boiled or allowed to stand and dry out over a night or weekend, further oxidation will occur, yielding the yellow ceric hydroxide.

Throughout any caustic metathesis, however, it must be remembered that, of the rare earths, any scandium present will largely pass into solution[5]. As will be emphasized subsequently, determination of scandium remains one of the most difficult problems in rare earth analysis. Scandium, it must be remembered, is amphoteric in nature and chameleon by intent. The possibility also exists that yttrium may exhibit some amphoteric characteristics[3], and thus traces of this element must be sought for carefully in the alkali filtrate. Similar care must be observed in those instances in which high lanthanum contents are to be expected.

Aluminium, tin, and pentavalent chromium will also appear in the alkali filtrate and again must be sought for therein, or their presence at least noted as possible contaminants of any scandium in solution.

Procedure: Weigh 2 g of finely comminuted mineral, ore, etc., into a 50 ml platinum dish. Add about 5 g of potassium or sodium bisulphate and fuse gently over a Meker flame. As the initial frothing diminishes, increase the heating rate and swirl the melt gently to detach any crusts from the side of the crucible. Continue heating until decomposition is complete (10–15 min). Allow the crucible and contents to cool and solidify in a slanting position in order to render the solid cake more easily detachable from the crucible. When cool, add a few drops of water to the crucible and warm gently to detach the cake. Place the crucible and its contents in a 400 ml beaker, cover with 150 ml of 5 per cent sulphuric acid, and boil to disintegrate the cake. Aid the break-up of the mass by gentle attrition from the end of a glass rod and, when the mass is completely disintegrated, remove and wash the crucible in a stream of hot water. Pour the hot suspension of the melt (and washings) into an excess of hot 10 per cent sodium hydroxide solution. Allow the suspension of hydroxides to stand, then decant and treat as for the sulphuric acid treatment (above).

HYDROCHLORIC ACID

Allanite, gadolinite, bastnaesite, etc., are easily decomposed by hydrochloric acid; the acid may also be employed for the dissolution of carbonates, hydroxides, and oxide materials obtained as process products. The basic exception and rule on the use of hydrochloric

acid as a solvent of oxides lies with the cerium content. That oxides of high cerium content are resistant to hydrochloric acid attack has long been known, and Brauer and Hagg[6] showed that the resistance to solubilization is essentially a function of the crystal structure of the oxide. Ceric oxide has an acid-resistant structure of the fluorite type, whereas the sesquioxides of the other rare earths adopt one or the other of the variations of the body centred cubic habit. Until 40 per cent cerium be present in the oxide mixture it is unable to impose its fluorite structure upon the cubic habit of the other rare earth oxides and is itself required to adopt the acid soluble cubic form. With cerium oxide contents above 40 per cent, however, the fluorite lattice predominates and the mixed oxides become increasingly resistant to attack by hydrochloric acid. When, therefore, more than 35 per cent of cerium is known, or expected, to be present in an oxide or mineral sample, hydrochloric acid should preferably not be employed. This criterion does not, of course, apply when carbonates, hydroxides, etc., are being considered.

At this point it may be remembered that boiling hydrochloric acid will decompose and dissolve the rare earth oxalates with the initial formation of oxalochlorides. Upon further digestion these decompose to the simple chlorides.

Because ceric chloride — $CeCl_4$ — is unknown and the hypothetical acid H_2CeCl_6 is very unstable, cerium in chloride solution may be considered to exist only in the tervalent state. Autoreduction similarly occurs when Pr^{4+} and Tb^{4+} oxides are dissolved in hydrochloric acid; in the case of these two elements, no valence states higher than 3+ have been found thus far in solution, regardless of the associated anion.

Mineral attack by hydrochloric acid will leave silica behind as a gelatinous residue, and dehydration by baking is then necessary to ensure its adequate removal from solution. In this process, dehydration of the rare earth chlorides will also occur together with the formation of the less soluble basic or oxychlorides. This can be avoided if dehydration be effected in a stream of hydrogen chloride, but under normal conditions a white, reluctantly soluble mass is obtained which has to be strongly treated to gain redissolution with dilute acid. Perseverance is here the keyword, and care should be taken to ensure that no rare earth chlorides remain with the insolubilized silica.