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Methodologies and Developments in the Analysis of REEs

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19.1 Introduction: Background and Driving Forces

The determination of concentrations of rare earth elements (REEs) continues to be important today in metallurgical, biological, medical, and environmental fields (Fujinawa 1992, Li et al. 2012, Miao et al. 2008, Li et al. 2011). At a time when the greatest advances in analytical methods are available, REEs' researchers and industries are looking for methods that will enable them to obtain reliable results in acceptable time frames and at low cost, which is challenging for some type of samples (Gorbatenko and Revina 2015, Fisher and Kara 2016, Balaram 2019). Here different techniques used in samples of different origins and in different states are compared. The methods described here include gravimetric, complexometric, spectrophotometric, and X-ray analysis methods.

19.2 Gravimetric and Volumetric Analyses

Gravimetric analysis, one of the classical quantitative chemical analytical methods, also called quantitative analysis by weight, involves the process of isolating and weighing an element or compound of known composition in pure form (Jeffery et al. 1989). The separation of the element or compound can be accomplished in a number of ways of which the most important methods are (i) precipitation methods, (ii) volatilization methods, (iii) electro analytical methods, and (iv) extraction and chromatographic methods (Jeffery et al. 1989). Despite the fact it is time-consuming, still gravimetry is recommended when the analyses demand highly accurate and

precise data. A large variety of anions and cations can be determined accurately by gravimetry. The determination of REEs by gravimetry involves precipitation, in which the REEs are precipitated as oxalates, hydroxides, or carbonates and are then determined quantitatively after calcination to give the oxides or complexometric titration with ethylenediaminetetraacetic acid (EDTA) (Bünzli and McGill 2019). Both methods can be used for group analysis or for the determination of a single element. Various types of chromatography are also used, with the advantage of providing simultaneous separation in the case of mixtures (Bünzli and McGill 2019).

Before the invention of sophisticated instruments, research efforts were mainly focused on the quantitative analysis of REEs by titrimetric methods. The determination of rare earths by titrimetric analysis increased dramatically after the introduction of polyaminocarboxylic acids (for example, EDTA, diethylenetriaminepentaacetic acid (DTPA), and triethylenetetraaminehexaacetic acid (TTHA)) in analytical chemistry (Pribil 1967, Pribil and Horacek 1967, Sangal et al. 1969, Fritz et al. 1958a, Gupta and Powel 1964). The sum of concentrations of the REEs or concentrations of individual rare earth ions were successfully determined using complexometric titrations with EDTA, DTPA, or TTHA in the presence of indicators such as xylenol orange, arsenazo, and methylthymol blue. The choice of indicator is dependent on pH of the solution. The concentration of stock solutions (generally having high concentrations around 0.1–1 mol/L) can be conveniently determined by complexometry with few time dilutions (Lyle and Rahman 1963).

The recommended method of complexometric titration with EDTA is briefly outlined here:

In a simple procedure, the REE solution pH is adjusted to 7.2, then three drops of pyridine and three drops of xylenol orange (0.45 mmol/L) indicator are added, and the solution is titrated with standard EDTA solution (Ramirez et al. 2007). The method can be slightly modified as: to a solution having 0.25–1 mmol: four to five drops of pyridine are added, then the pH is adjusted to 5.5–6.5 with aqueous ammonia or dilute acid solution, two drops of arsenazo (0.5%) indicator are added, and the solution is titrated with standard EDTA solution (Fritz et al. 1958a). Lyle and Rahman concluded that xylenol orange exhibited satisfactory results in direct titrations (Lyle and Rahman 1963).

19.3 Spectrophotometry

The quantitative determination of REEs by UV–VIS spectrometer is based on the characteristic absorption bands in UV–VIS region due to the electronic transitions in the 4f shell (Sastri et al. 2003). The sensitivities can be as low as 0.1 mg/mL. The aim of the determination of REEs by spectrophotometry is to develop a method that is highly selective, sensitive, fast, and easily reproducible without excessive control of experimental conditions. Fritz et al. developed a colorimetric method using arsenazo I as coloring agent for the determination of REEs from aqueous solutions (Fritz et al. 1958b). The method is described as follows: To a sample solution containing 0.0002–0.001 mmol, 2 mL of arsenazo I and 5 mL of triethanolamine (or three drops

of pyridine) are added, and the pH is adjusted to 8.0 and measured against the reagent blank (Fritz et al. 1958b). In another method, 3 mL of 0.45 mmol/L xylenol orange indicator is added to the REE solution (0.25–0.003 mmol/L) in a 10 mL flask and made up with acetic acid–ammonia buffer solution of pH 6, and then the absorbance is measured in the spectrophotometer (Ramirez et al. 2007). The analysis of REEs, either in total or individual REEs, using arsenazo III is also one of the most practiced methods. In weakly acidic media, REEs react with arsenazo III to form colored compounds which is the basis of this sensitive method. The procedure is described as follows: 1 mL of 1% ascorbic acid solution is added to the REE solution containing less than 0.04 mg of REE at pH ~1. To this, 2 mL of formate buffer (pH 3.5) and 3 mL of arsenazo III are added. The pH of the solution is adjusted to 2.6 ± 0.1 . The absorbance is measured at 650 nm (Marczenko and Balcerzak 2000).

Most of the developed methods for the determination of REEs discussed about the analysis from aqueous solutions. However, few attempts have been made to measure from organic samples as well. A simple and direct spectrophotometric method was developed to measure the concentrations of REEs in organic extracts of commonly used solvent extraction reagents such as di-2-ethylhexylphosphoric acid (D2EHPA) and trioctylamine (TOA). The sample preparation method is briefly outlined here: to an organic sample of REEs containing less than 25 μg , n-butanol is added until a homogeneous phase is obtained, and then 5 mL of chlorophosphonazo solution in

n-butanol is added. The absorbance of this solution is measured against its reagent blank (Vilimec and Jakubec 1987).

19.3.1 Atomic Absorption Spectrometry (AAS)

Atomic absorption spectrometry (AAS) using different types of flame sources, such as flame AAS (FAAS) and graphite furnace AAS (GFAAS), is also useful for the determination of REEs (Rao and Biju 2000). AAS equipped with nitrous oxide–acetylene flame has been used for the measurement of several REEs in alloys, steels, rocks, and ores. However, FAAS is less sensitive. On the other hand, GFAAS, which is more sensitive than FAAS, suffers from interference due to matrix. GFAAS is employed for REEs' determination in sea water, geological samples, rocks, soils, slags, etc. (Rao and Biju 2000). AAS allows the measurement of one element at one time. Considering the time taken for analysis and availability of other simultaneous multi-element measurement instruments, AAS is scarcely used for REEs in recent times.

19.3.2 Microwave Plasma Atomic Emission Spectrometer (MP-AES)

Microwave plasma atomic emission spectrometer (MP-AES) is a new commercial instrument in the analysis of REEs introduced in 2011. The running costs of MP-AES seem to be less than those of inductively coupled plasma optical emission spectroscopy (ICP-OES) since the microwave plasma is generated by using nitrogen gas (Balaram 2019). Helmeczi et al. showed that the

analyses of results after digestion by MP-AES and inductively coupled plasma mass spectrometry (ICP-MS) are identical proving that MP-AES is an efficient instrument to quantify REEs (Helmeczi et al. 2016). A variety of samples, industrial effluents, water, soils, rocks and ores, sediments have been analyzed by MP-AES during recent years. It appears to be an attractive alternative to FAAS and ICP-OES (Balaram 2019).

19.4 Flame and Plasma Atomic Absorption and Emission (ICP-OES/ICP-MS)

The most successful instrument for the determination of REEs in low concentrations is the modern inductively coupled plasma (ICP) spectrometer. Acidified diluted aqueous samples can be measured straightforward. However, organic liquid samples and aqueous samples with high matrix content cannot be reliably determined by this modern equipment. In the case of solid samples, e.g., geological (soils, rocks) and biological (animal, plant) samples, the REEs are measured after (microwave-assisted) acid digestion (0.1–1 g sample) with different mixtures of acids and oxidizers. The mixtures of acids, time, temperature, and number of cycles to be employed are more or less aggressive, depending on whether the aim is to know the total concentration or to know only the fraction which is labile, bioavailable (in which case not a “full” but a “partial” extraction of REEs is aimed). Following the digestion, acidified water is added until a known final volume (25–50 mL) is obtained, and the solution is filtered.

Even though ICP is one of the techniques with the lowest detection limit (10 ppb), sometimes the REEs of interest are present below that limit. In such cases, several solid phase preconcentration methods exist, such as the absorbent hydroxyl multi-wall carbon nanotubes which lower the detection limits up to 0.3–1.2 ng L⁻¹ and the relative standard deviations to <5% (Zhang et al. 2016). Other analytical practices that have been coupled together with ICP in order to match the different applications and gain more confidence on the instrumental method are laser ablation (LA) for continuous compositional spatial profiles with high resolution (Hsieh et al. 2011), cloud point extraction (CPE) with a chelating agent in flow injection analysis associated to ICP (Li and Hu 2010), and sector field (SF) and/or multicollector (MC-ICP) for high-sensitivity detection, speciation analysis, and isotope study at the molecular level (Moldovan et al. 2004, Rousseau et al. 2013).

19.5 X-Ray Excited Optical Fluorescence (XEOF) Spectrometry and X-Ray Fluorescence (XRF) Spectrometry

X-ray excited optical fluorescence (XEOF) spectrometry and cathode-ray excited emission spectrum focus on trace analysis of REEs, but they could not be established for routine analysis. However, X-ray fluorescence (XRF) (secondary emission) is used routinely for all sample types (liquids, powders, metals, or fused beads), including those specially challenging such as hydrophobic liquids and samples with high matrix content. The measurable concentration of REEs

ranges from 100% down only to absolute 0.01% (100 ppm) when using spectrometers equipped with wavelength-dispersive optics. Spectrometers with energy-dispersive detection technique were not available.

When the incidence angle of X-ray is very low (critical angle 0.1° for Mo-K α X-rays), the total reflection X-ray fluorescence (TXRF) occurs. This decreases the background signal and the low detection limits (ppm, sometimes ppb). The low incident angle also implies excitation by the incident and reflected X-rays, and location of the sample being very close to the detector. Aqueous and organic liquids as well as solids can be analyzed qualitatively (e.g., ratios) and quantitatively (suspensions, matrix effects) by either internal standards (based on relative intensities) or external standards (based on absolute intensities) by TXRF. Wafers are the main samples in industrial application. Proper calibration of the sensitivity factors may be necessary for some elements, even when TXRF manufacturers claim that the sensitivity factors do not change. The sample preparation procedure should be closely followed, especially for liquid samples (small volumes (μL instead of mL), sample drop in the middle of the previously siliconized carrier) (Riaño et al. 2016). In the case of a sample with no matrix content, the choice of the internal standard does not matter, while in the case of a sample with matrix, the standard should have a value of energy of the measured XRF line similar to that of the analyte, with a concentration close to that of the analyte (Hellin et al. 2005). To prevent any inhomogeneous accumulation of mass such as fractional crystallization of hydrolyzing species during the drying step, alcohols and surfactants are used as stabilizing

agents to spread and homogenize the samples with high inorganic salt or non-volatile organic liquid contents (Regadío et al. 2017).

19.6 Mass Spectrometry and Isotope Dilution and Neutron Activation

(NA) Analysis

Mass spectrometry (and isotope dilution) is a method that can be applied for trace REE analysis and is preferred for the analysis of small samples. There are different instruments with different ion sources, depending on which the sample preparation varies. The low limit of detection is 0.1 ppm.

Neutron activation (NA) is used for analyses of REE in reactor materials and metals; high-purity chemicals; and geological, biological, and water samples. It is characterized by high sensitivity for most of the elements, good specificity and is free from reagent contamination. Similar to TXRF, NA can handle matrix effects and provide a multi-element determination. Even though, it was the first technique for studying trace elements in geological samples; nowadays its importance and use have dropped due to emerging, new analytical techniques.

19.7 Comparison and Assessment

Only the most widely used methods in recent times were considered in this last section for comparison, since the older methods such as gravimetry, complexometry and UV-VIS are not much in use. The selection of a proper method depends on various variables that are compiled in **Table 19.1**. The person concerned should ponder which ones are more important and take the final decision. The two preferred methods for routine analyses are ICP and TXRF (**Figures 19.1** and **19.2**). The former provides slightly better quality data and lower low detection limits, but the latter can deal better with samples containing high concentration of inorganic salt and hydrophobic, non-volatile, organic liquids. Specifically, for geological rock samples, XRF after pulverization of the sample is more advisable, because silicates are difficult to dissolve by acid digestion, showing greater deviations between different acid-digested replicates analyzed by ICP than with XRF (**Figure 19.3**). The drawback is the much higher low detection limit of XRF compared to ICP, losing sensitivity.

Table 19.1 Overview and Assessment of the Methodologies in the Analysis of REEs

	ICP	XRF	TXRF
User interface & operator training ^a	☹	☺	☺
Sample preparation time ^b	2 h (dl + cl) excl AD when solid or organic	<0.2 h (pulv)	1 h (dl + dr)
Measurement time	100 s	A few seconds	300 s
Calibration ^c	Daily	Yearly. Lib	Yearly (except new matrices)
Organic samples ^d	Difficult: fol AD digestion when possible	Only solid samples	Yes
Solids ^e	Destr (LA, AD, AF)	Non-destr	Non-destr
Samples with matrices	Difficult	Yes (solid samples)	Yes
Low limit of detection	ppm/ppb	100 ppm	ppm
Sample amount ^f	<i>M</i>	<i>s</i>	<i>s</i>
Element analysis ^g	Multi – all REE	Multi – all REE	Multi – all REE
Lab space ^h	L	S (handheld analyzer)	S
Cost of the machine	200 000 €	20 000 €	100 000 €
Operation cost ⁱ	€ € € (gas/nebulizer)	€	€€ (X-ray source/detector)

^a☺: Easy, ☺: moderate, ☹: difficult. ^bdl, dilutions; dr, drying; cl, calibration; excl, excluding, AD, acid digestion, pulv, pulverization. ^cLib, (extensive grade) libraries to match a wide range of different applications. ^dfol, following. ^edestr, destructive; LA, laser ablation (spatial profiles); AF, alkali fusion. ^f*s*, small; *m*, medium; *l*, large. ^gMulti, simultaneous multi-element analysis. ^h**S**, small; **M**, medium; **L**, large. ⁱ€, small cost; €,€, medium cost; €€, high cost.

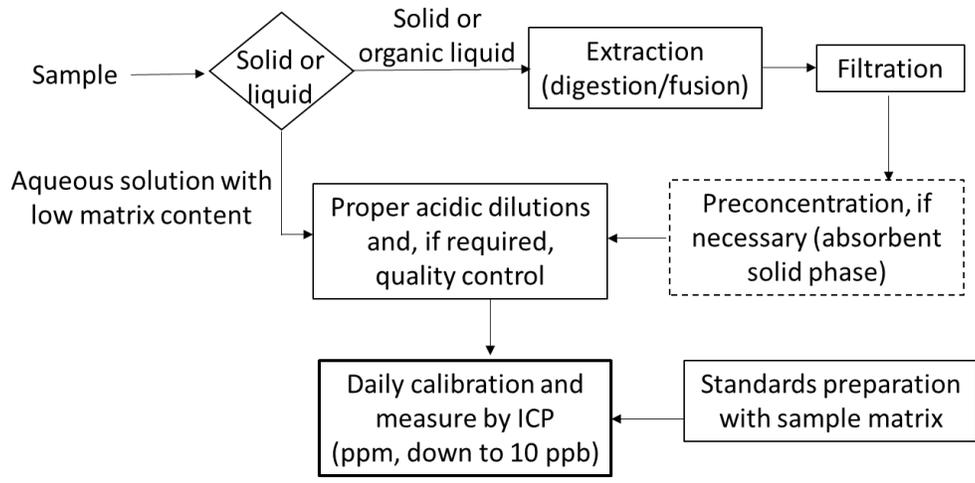


Figure 19.1 Flowsheet with the analytical steps for ICP analyses.

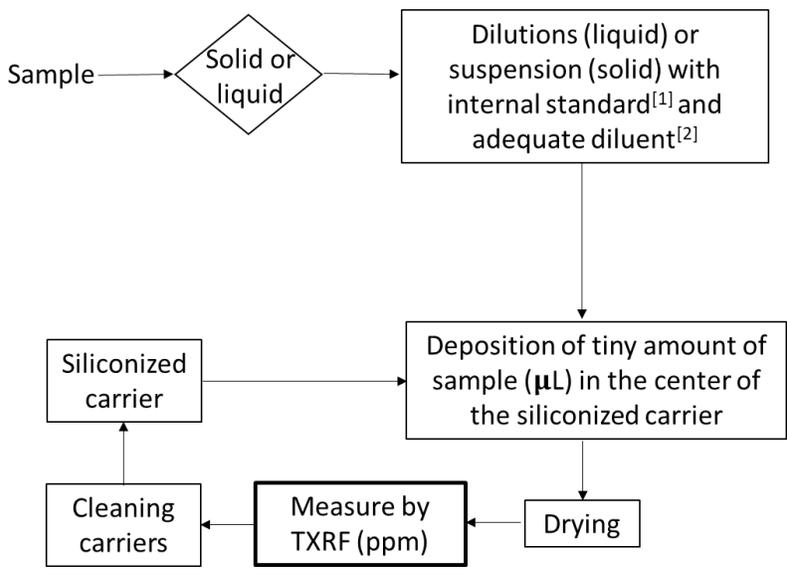


Figure 19.2 Flowsheet with the analytical steps for TXRF analyses. For solid, organic liquid, or high matrix content, ^[1]use internal standards with energy of the measured XRF line similar to that of the analyte and with a concentration close to that of the analyte and ^[2]use homogenizing–stabilizing agents as diluents.

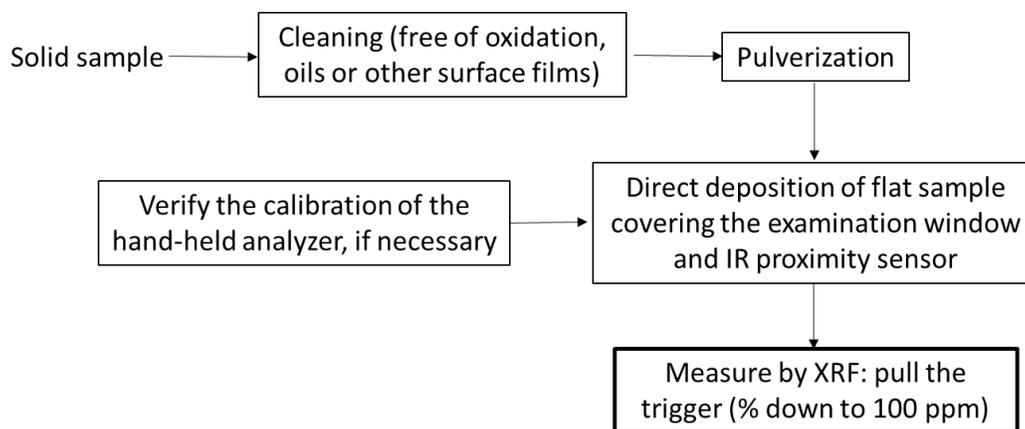


Figure 19.3 Flowsheet with the analytical steps for handheld XRF analyses.

REFERENCES

Balaram, V. 2019. Rare earth elements: A review of applications, occurrence, exploration, analysis, recycling, and environmental impact. *Geoscience Frontiers*. doi:

10.1016/j.gsf.2018.12.005.

Bünzli, J.-C.G., and McGill, I. 2019. Rare earth elements. In *Ullmann's Encyclopedia of Industrial Chemistry*. doi: 10.1002/14356007.a22_607.pub2.

Fisher, A., and Kara, D. 2016. Determination of rare earth elements in natural water samples – A review of sample separation, preconcentration and direct methodologies. *Analytica Chimica Acta* 935:1–29. doi: 10.1016/j.aca.2016.05.052.

Fritz, J.E., Oliver, R.T., and Pietrzyk, D. J. 1958a. Chelometric titrations using an azoarsonic acid indicator. *Analytical Chemistry* 30:1111–1114.

Fritz, J.E., Richard, M.J., and Lane, W.J. 1958b. Spectrophotometric determination of rare earths. *Analytical Chemistry* 30:1776–1779.

Fujinawa, A. 1992. Distinctive REE patterns for tholeiitic and calc-alkaline magma series co-occurring at Adatara volcano, Northeast Japan. *Geochemical Journal* 26 (6):395–409. doi: 10.2343/geochemj.26.395.

Gorbatenko, A.A., and Revina, E.I. 2015. A review of instrumental methods for determination of rare earth elements. *Inorganic Materials* 51 (14):1375–1388. doi: 10.1134/s0020168515140058.

Gupta, A.K., and Powel, J.E. 1964. Successive determination of thorium and rare earths by complexometric titrations. *Talanta* 11:1339–1342.

Hellin, D., Rip, J., Geens, V., Delande, T., Conard, T., De Gendt, S., and Vinckier, C. 2005. Remediation for TXRF saturation effects on microdroplet residues from preconcentration methods on semiconductor wafers. *Journal of Analytical Atomic Spectrometry* 20 (7):652–658. doi: 10.1039/B502208H.

Helmecci, E., Wang, Y., and Brindle, I.D., 2016. A novel methodology for rapid digestion of rare earth element ores and determination by micro wave plasma-atomic emission spectrometry and dynamic reaction cell-inductively coupled plasma-mass spectrometry. *Talanta* 160:521–527.

Hsieh, H. F., Chen, Y.H., and Wang, C.F. 2011. A magnesium hydroxide preconcentration/matrix reduction method for the analysis of rare earth elements in water samples using laser ablation inductively coupled plasma mass spectrometry. *Talanta* 85 (2):983–990. doi: 10.1016/j.talanta.2011.05.011.

Jeffery, G.H., Bassett, J., Mendham, J., and Denney, R.C. 1989. *Vogel's Textbook of Quantitative Chemical Analysis*. Harlow: Longman Scientific & Technical.

Li, M. H., Zhu, L.P., Wang, J.B., Wang, L.Q., Yi, C.L., and Galy, A. 2011. Multiple implications of rare earth elements for Holocene environmental changes in Nam Co, Tibet. *Quaternary International* 236:96–106. doi: 10.1016/j.quaint.2010.12.022.

Li, Y. J., and Hu, B. 2010. Cloud point extraction with/without chelating agent on-line coupled with inductively coupled plasma optical emission spectrometry for the determination of trace rare earth elements in biological samples. *Journal of Hazardous Materials* 174 (1–3):534–540. doi: 10.1016/j.jhazmat.2009.09.084.

Li, Y., Yang, J.L., and Jiang, Y. 2012. Trace rare earth element detection in food and agricultural products based on flow injection walnut shell packed microcolumn preconcentration coupled with inductively coupled plasma mass spectrometry. *Journal of Agricultural and Food Chemistry* 60 (12):3033–3041. doi: 10.1021/jf2049646.

Lyle, S.J., and Rahman, Md.M. 1963. Complexometric titration of yttrium and the lanthanons. A comparison of direct methods. *Talanta* 10:1177–1182.

Marczenko, Z., and Balcerzak, M., 2000. *Separation, Preconcentration and Spectrophotometry in Inorganic Analysis*. Amsterdam: Elsevier.

Miao, L., Xu, R.S., Ma, Y.L., Zhu, Z.Y., Wang, J., Cai, R., and Chen, Y. 2008. Geochemistry and biogeochemistry of rare earth elements in a surface environment (soil and plant) in South China. *Environmental Geology* 56 (2):225–235. doi: 10.1007/s00254-007-1157-0.

Moldovan, M., Krupp, E.M., Holliday, A.E., and Donard, O.F.X. 2004. High resolution sector field ICP-MS and multicollector ICP-MS as tools for trace metal speciation in environmental studies: A review. *Journal of Analytical Atomic Spectrometry* 19 (7):815–822. doi: 10.1039/B403128H.

Pribil, R. 1967. Present state of complexometry-IV* Determination of rare earths. *Talanta* 14:619–627.

Pribil, R., and Horacek, J. 1967. Contributions to the basic problems of complexometry-XXIII. Determination of thorium, scandium and some lanthanides in the presence of each other. *Talanta* 14:313–316.

Ramirez, E.F., Reyes, M.J., and Rios, M.J.S. 2007. Stability constants of chloride complexes of lanthanum. *Journal of Chemical and Engineering Data* 52:373–376.

Rao, T.P., and Biju, V.M., 2000. Trace determination of lanthanides in metallurgical, environmental, and geological samples. *Critical Reviews in Analytical Chemistry*. 30:179–220.

Regadío, M., Riaño, S., Binnemans, K., and Hoogerstraete, T.M. 2017. Direct analysis of metal ions in solutions with high salt concentrations by total reflection X-ray fluorescence. *Analytical Chemistry* 89 (8):4595–4603. doi: 10.1021/acs.analchem.7b00097.

Riaño, S., Regadío, M., Binnemans, K., and Hoogerstraete, T.M. 2016. Practical guidelines for best practice on total reflection X-ray fluorescence spectroscopy: Analysis of aqueous solutions. *Spectrochimica Acta Part B: Atomic Spectroscopy* 124:109–115.

Rousseau, T.C.C., Sonke, J. E, Chmeleff, J., Candaudap, F., Lacan, F., Boaventura, G., Seyler, P., and Jeandel, C. 2013. Rare earth element analysis in natural waters by multiple isotope dilution – sector field ICP-MS. *Journal of Analytical Atomic Spectrometry* 28 (4):573–584. doi: 10.1039/c3ja30332b.

Sangal, S.P., Agarwal, B.V., and Deay, A.K., 1969. Complexometric determination of rare earths in aqueous solutions. *Microchimica Acta* 57:660–663.

Sastri, V.R., Perumareddi, J.R., Ramachandra Rao, V., Rayudu, G.V.S., and Bünzli. J.-C.G. 2003. *Modern Aspects of Rare Earths and Their Complexes*. Amsterdam: Elsevier.

Vilimec, J., and Jakubec, K., 1987. Direct spectrophotometric determination of rare earths in organic extracts with chlorophosphonazo III. *Microchemical Journal* 35:325–327.

Zhang, J. Y., Wang, X.I., Dong, Y.H., Xu, Z.F., and Li, G.M. 2016. Solid phase extraction of rare earth elements in deep groundwater with multi-wall carbon nanotubes as adsorbent for the determination by inductively coupled plasma mass spectrometry. *Atomic Spectroscopy* 37 (1):1–6.