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Application of ICP AES to the determination of REE in Egypt's black sand deposits

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Abstract

A method has been developed for the direct determination of seven REE and yttrium in black sand concentrate samples by inductively coupled plasma atomic emission spectrometry. The samples represent three different areas of Egypt's Mediterranean Coast. The results revealed the presence of considerable reserves of REE in these deposits.

1. Introduction

In Egypt, black sands of economic importance are deposited in large stretches along the Mediterranean Coast extending from Abu Qir Bay, east of Alexandria to Rafah, the eastern boarder of Egypt (Fig. 1). These black sands are derived from the upper reaches of the Nile, mostly from the Ethiopia Volcanic highland and Sudan, and are deposited at the river mouths where the flow velocity is reduced. For several years, various studies have been carried out by different investigators and organizations to assess the economic mineral constituent of these black sands in different areas [1]. The most attention was given to the Rashid (Rosetta) area as it has the richest occurrence of black sands with the highest concentration of heavy minerals. Later, other areas such as the Arish and Rommana areas were investigated.

Recently, the Egyptian Geological Survey and Mining Authority (EGSMA) planned a long term program to assess the black sand deposits along the Mediterranean coast of Egypt from Rashid to Rafah. This program started in the area east of the Rashid where a 18-km plot was studied followed by a similar area west of Arish. Now, an area of 20-km at Rommana is under investigation. The results achieved up to now can be briefly summarized as follows:

1. The reserves of black sands in the areas investigated amount to 565 million tons in the Rashid area and 45 million tons in the Arish area representing concentrate reserves of 9.3 and 1.4 million tons in the two areas, respectively.
2. Ilmenite is the main constituent among the economic minerals in the areas investigated. Other economic minerals in decreasing order of abundance are magnetite, hematite, zircon, garnet, monazite and rutile.
3. The REE ore monazite represents one of the most important economic minerals found in the black sands.

These investigations initiated interest in developing a technique using inductively coupled plasma atomic emission spectrometry (ICP AES) for the determination of REE in black sand samples. Such a technique would help in estimating the reserves of REE in these deposits; also, it can give an idea of the content of monazite in a black sand deposit. ICP AES has proved its applicability in the determination of REE in ores and minerals and various geological materials [2–4].

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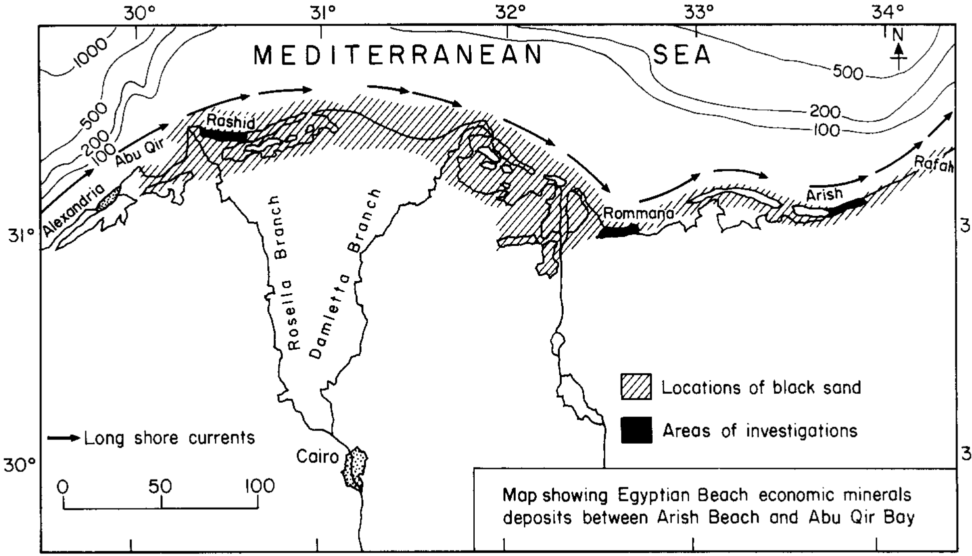

Fig. 1. Map of the Nile Delta.

2. Experimental details

2.1. Instrumental facilities and operating parameters

Table 1 lists the instrumental facilities and the operating parameters of the ICP used in this study.

2.2. Samples and sample dissolution procedures

In the present work, three black sand samples were considered for investigation. They represent the three areas mentioned above, namely Rashid, Rommana and Arish. Various dissolution procedures have been tried to achieve complete dissolution of the samples before introduction to the ICP. No complete dissolution could be achieved using either open or closed vessel acid digestion procedures. For this reason, a fusion procedure was applied. The dissolution procedures tested were as follows.

2.2.1. Procedure I: Fusion with sodium carbonate

A sample of 0.25 g was fused with 1.5 g Na_2CO_3 in a platinum crucible over a Meker burner. The crucible was then transferred to a muffle furnace and heated for 2 h at 900 °C. After cooling, the cake was transferred carefully with 10 ml 50% HCl to a beaker and heated on a hot plate to near dryness. The residue was then treated with a mixture of 10 ml of concentrated HNO_3 and 10 ml of concentrated HCl and evaporated until the volume was reduced to about 2 ml. Distilled water was then added to the residue, which dissolved on

TABLE 1. Instrumental facilities and operating parameters

ICP equipment	
RF generator	FS-4 generator (Linn), 27.12 MHz free running, 4 kW maximum output power, 750 W ICP power
Plasma torch	Greenfield
Nebulizer	GMK Babington (Labtest)
Gas flows	Cooling gas: 16 l min^{-1} argon Plasma gas: 3 l min^{-1} argon Carrier gas: 3 bar (argon) observation
Height	12 mm above the load coil
Spectrometric arrangement	
Monochromator	Model 2051 (McPherson)
Mounting	Czerny Turner, focal length 1 m
Grating	1200 grooves, plane reciprocal linear
Dispersion	0.83 nm mm^{-1} in the first order
Slits	0.02 mm entrance, 0.02 mm exit
Photomultiplier	Hamamatsu R 300
Readout system	Linear mode of Model 762 McPherson Logarithmic Ratiometer, strip chart recorder Model 7172A (Hewlett Packard)

heating to produce a clear solution. The solution was diluted to 100 ml.

2.2.2. Procedure II: Closed acid digestion followed by a fusion step

To 0.25 g of sample, 1.5 ml HF, 0.5 ml HNO_3 and 0.5 ml HCl were added. The mixture was heated in a PTFE pressure decomposition vessel (Berghoff) for 15 h. The contents of the vessel were then transferred with 10 ml HF into a PTFE beaker to which 5 ml HNO_3 and 5 ml HCl were added and the mixture was evaporated to near dryness. The residue was treated with 5 ml HNO_3 and 3 ml $HClO_4$ and evaporated. Finally, 5 ml HNO_3 were added and the mixture heated until the volume was reduced to about 1 ml; distilled water was then added and the mixture filtered.

The undissolved residue was dried and fused with 0.5 g Na_2CO_3 in a platinum crucible on a Meker burner, and then heated for 2 h in a muffle furnace at 900 °C. After cooling, the cake was transferred with 10 ml 50% HCl into a beaker and evaporated to near dryness. The residue was then treated with 5 ml HNO_3 and 5 ml HCl and the mixture was heated until the volume was reduced to about 1 ml. Distilled water was added and heating was continued until the residue dissolved completely. The solutions from the two steps were combined and diluted to 100 ml.

2.2.3. Procedure III: Open acid digestion followed by a fusion step

To 0.25 g of sample, 15 ml HF, 5 ml HNO_3 and 5 ml HCl were added in a PTFE beaker. The mixture was heated on a hot plate and evaporated to near dryness. Subsequently, 5 ml HNO_3 and 3 ml $HClO_4$ were added and the mixture was evaporated again to near dryness. A further 5 ml HNO_3 was added and heating was continued until the volume was reduced to about 1 ml. Distilled water was added and the solution filtered. The undissolved residue was dried and fused with 0.5 g Na_2CO_3 and the procedure was completed as in procedure II.

3. Results and discussion

3.1. Matrix effect of sodium

The effect of an easily ionizable element (EIE) on the intensities of spectral lines emitted by an ICP has been studied by various investigators [5]. In the upper regions of the analyte channel, the addition of excess EIE, in general, causes depression of emission intensity for both atom and ion lines.

In the present work, the sample solutions contained excess amounts of sodium. For this reason, it was found important to study the effect of sodium on the intensity of REE spectral lines and to optimize the working conditions. For this study, the spectral lines La^{II} 408.672 nm and Ce^{II} 446.021 nm were taken as test lines and the effect of increasing sodium concentration on their intensity was determined. The results obtained are shown in Fig. 2. It can be seen that at the level of Na concentration in the sample solution, a depression in intensity of about 16% for the La line and 13% for the Ce line is to be expected. These results suggest that sodium should be added to the calibration solutions in the same concentration as that in the sample solutions, to compensate for matrix effects.

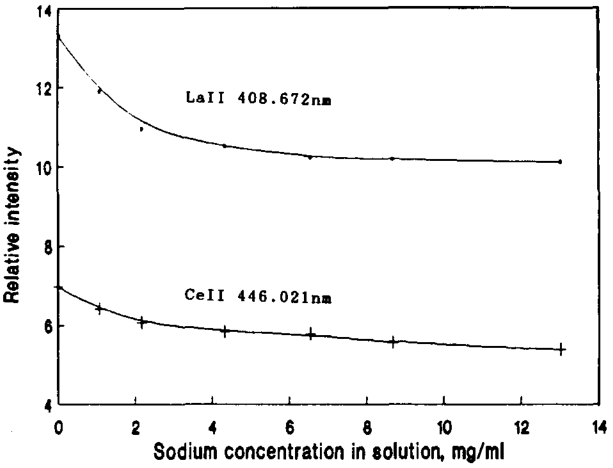

Fig. 2. Effect of increasing sodium concentration on RE spectral lines.

3.2. Analytical wavelengths and analytical figures of merit

For the selection of analysis of REE spectral lines, detailed studies on the suitability of the many lines available for each element were carried out. Available data on line overlap interferences, which may suffer by a selected line from other REE, as well as from the major elements in the sample solution, were consulted [6,7]. In addition, previous experience gained in this laboratory in determining REE in phosphate samples was utilized [3,4]. Moreover, to ensure the freedom of a selected spectral line from line overlap interference originating from the major constituents of the samples, namely Ti, Fe and Zr, solutions of these elements in concentrations matching their concentrations in the sample solutions were scanned in the wavelength region of the analysis line. The absence of emission signals at the wavelength of the analysis line ensured the suitability of the REE line for analysis. For some REE, specially those present at low concentrations, the most sensitive lines were found to suffer serious interferences so that their determination was impossible. These elements were Tb and Ho. On the other hand, for the elements Pr, Gd, Yb and Lu, the intensity of the

TABLE 2. Wavelength of analysis lines, limits of detection C_L, precision of intensity measurement (RSD) and interferents

Element		Wavelength (nm)	C_L (μg/ml)	RSD (%)	Interferent
La	II	398.852	0.02	2.3	
	II	406.672	0.04	2.7	
Ce	II	413.765	0.20	2.4	
	II	446.021	0.29	4.5	
Pr	II	390.844	0.17	2.5	Ce^{II} 390.841
Nd	II	430.358	0.14	2.7	
	II	406.109	0.16	2.6	
Sm	II	359.260	0.15	3.0	
Eu	II	412.970	0.009	2.5	
Gd	II	342.247	0.05	2.8	Fe^{II} 342.249
Tb	II	350.917	0.06	2.9	Zr 350.932 +
Dy	II	353.170	0.03	3.3	
Ho	II	339.898	0.05	4.0	Zr^{II} 339.935 + Ti^{I} 339.863 +
Er	II	369.265	0.04	1.8	
Tm	II	346.220	0.08	2.0	
Yb	II	328.937	0.003	3.1	V^{II} 328.939
Lu	II	261.542	0.008	0.6	Fe^{I} 261.542 V^{II} 261.541
Y	II	360.073	0.01	1.4	

interfering lines were at the level that permits correction. For this reason, the concentrations of the interfering elements, namely Fe, Ti and Zr in addition to Ce, were measured in the sample solutions. The concentration of Er and Tm in the sample solutions were within their limits of detection and therefore could not be evaluated. The wavelengths of the selected analysis lines are given in Table 2.

The limits of detection attainable with the selected REE lines, based on $3\sqrt{2}$ times the standard deviation of the background intensity, are also listed in Table 2. The latter was determined from the peak to peak intensity of the background obtained from the scan of the wavelength region of the considered spectral line using a solution containing an appropriate concentration of the element and sodium concentration matching that in the sample solutions.

Table 2 also lists the precision of the intensity determination calculated as the relative standard deviation (RSD) of 10 determinations of the net intensity of the spectral line. Fluctuations originate mainly from the nebulization process.

3.3. *Evaluation of the sample dissolution procedures*

For the evaluation of the three dissolution procedures used, five replicates of the Rashid sample were dissolved using each procedure. Table 3 gives the results obtained for the average concentration of the elements La, Ce, Nd and Y in this sample and the RSD obtained from the analysis of the five replications. From the table, it can be seen that decomposition using the closed acid digestion procedure followed by fusion of the residue with Na_2CaO_3 (procedure II) yields the highest values of concentration of the measured elements and the lowest values of RSD, which indicate its effectiveness for the dissolution of this type of sample. Therefore, these results are used in the rest of this work. The relatively low values of element concentrations with the higher value RSDs obtained with the fusion procedure (procedure I) may be related to the higher amounts of Na_2CO_3 used in this procedure with its adverse effect on the nebulization process.

TABLE 3. Results obtained for REE in the Rashid sample by different dissolution procedures

Element	Dissolution procedure					
	I		II		III	
	C (μg/g)	RSD (%)	C (μg/g)	RSD (%)	C (μg/g)	RSD (%)
La	1075 ± 64	6.0	1257 ± 39	3.1	1254 ± 64	5.1
Ce	1894 ± 123	6.5	2151 ± 60	2.8	2092 ± 124	6.0
Nd	964 ± 69	7.2	972 ± 49	5.0	944 ± 58	6.2
Y	328 ± 19	5.8	380 ± 10	2.5	374 ± 19	5.2

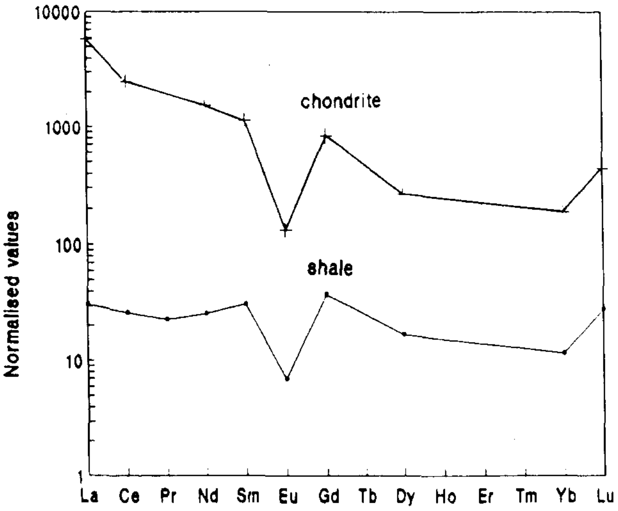

Fig. 3. Chondrite and shale normalized REE pattern for the Rashid sample.

3.4. *Results of the analysis of the black sand samples*

For the determination of REE in the samples under investigation, calibration solutions containing Na in a concentration matching its concentration in the sample solutions were used. For black sands, there were no standard reference samples available. For this reason, a check of the accuracy of the technique was carried out by performing additional measurements. Determinations using more than one spectral line were performed for those elements for which more than one

TABLE 4. Results of analysis of black sand samples for REE

Element	Concentration (μg/g)		
	Rashid	Rommana	Arish
La	1257	342	84
Ce	2151	560	196
Pr	193	65	–
Nd	972	230	82
Sm	231	65	–
Eu	11.7	–	–
Gd	233	98	35
Dy	92	39	25
Yb	41	30	12
Lu	15	12	5
Y	380	200	95
Total	5576.7	1641	534

sensitive interference-free spectral line was available. These are La, Ce, Nd, Sm. The good agreement of the results indicates the accuracy of the measured concentrations. Moreover, chondrite and shale normalized patterns [8] were constructed for the Rashid sample. The patterns are shown in Fig. 3. The smooth patterns obtained indicate the credibility of the technique. However the patterns show Eu deficiency and unexpected high values for Lu. The results obtained for the three black sand samples under investigation are given in Table 4.

4. Conclusions

From the results obtained in this work, the following conclusions can be made. The ICP AES technique can be applied for the accurate determination of Y and seven REE in black sand samples without any separation or preconcentration of these elements. The sum of REE and Y measured in the samples under investigation represent 5.58, 1.64 and 0.53 mg/g of the Rashid, Rommana and Arish samples, respectively. The black sands in the investigated areas represent only about 5% of the black sand reserves in Egypt. Accordingly, it can be concluded that these deposits represent considerable reserves of REE. Since the origin of REE in these samples is monazite, the sum of the determined elements constitute at least 98% of the total REE content of these samples. Accordingly, the knowledge of the sum of these elements in a black sand sample can be used to estimate the content of monazite in the sample without the need for separation of monazite.

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