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ION CHROMATOGRAPHIC DETERMINATION OF YTTRIUM AFTER SEPARATION FROM DYSPROSIUM SIMULTANEOUSLY WITH INDIVIDUAL QUANTIFICATION OF RARE EARTH ELEMENTS

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ABSTRACT

A particular ion chromatographic method for yttrium determination after separation from dysprosium simultaneously with individual quantification of rare earth elements has been modified. Selective separation of yttrium from dysprosium plus the other thirteen rare earth elements was achieved by gradient elution using oxalic / diglycolic acid eluent mixture on IonPac CS5A separating column. The separated ions were then detected using 4-(2-pyridylazo)resorcinol (PAR) at 530 nm. The optimized method was subsequently validated by the analysis of a reference sample from Abu Rusheid area followed by its application on two geological materials from Wadi Khuda-Wadi Shut area and Abu Tartour phosphate deposits. Relative standard deviation (RSD) calculated for the analyzed samples were expressed with very low values the matter which confirms the precision of the developed method. The present work allowed the individual determination of lanthanide elements including yttrium and six heavy metal ions in an absolute time of about 110 minutes.

Keywords: Ion chromatography; Yttrium; Rare Earth Elements; Heavy Metals; Gradient Elution.

1. INTRODUCTION

Yttrium represents one of the rare earth elements which involve the 15 elements plus scandium [1]. It is quite often existed in nature with the lanthanides in rare earth minerals and which by no means finds as a free element [1]. Yttrium is a most significant element in frequent protruding industrial manufactures of electronics, lasers, phosphors, superconductors, and in a variety of therapeutic purposes [2]. It is additionally broadly utilized in astronavigation, nuclear energy and metallurgical industries [3]. The application of yttrium relies on its features as well as on its purity, coming about a considerable raise in the cost with request on virtue [4].

Yttrium (Y) looks like terbium (Tb) and dysprosium (Dy) in its chemical reactivity [5]. Despite the fact that lanthanides found one row below yttrium in the periodic table, the likeness in atomic radius might be credited to the lanthanide contraction [3].

The separation of yttrium from the rare earth elements REEs is extremely difficult and considered a challenging problem owing to their similar charge and ionic radii, for

example, Y elutes very close to Dy and Ho [3,6,7]. This co-elution phenomenon interferes with the precise determination of Y, Dy and Ho [8]. Separation of the REEs can only be accomplished by employing complexing agents in the mobile or stationary phases, which depends on the differences in stability constants of the metal complexes [9]. Consequently, trials have been done to create or develop chromatographic methods which involves REEs separation with elution order doesn't obey that of their ionic radii. Examples of such systems involves ion chromatographic separation using sulfonic acid as a resin and nitrilotriacetic acid (NTA; $N(CH_2CO_2H)_3$) solution as an eluent [10], conventional cation exchange chromatography utilizing also sulfonic acid resin and hydroxy ethylenediaminetetraacetate (HEDTA) eluent [11]. Furthermore, reversed phase-high performance liquid chromatography (RP-HPLC) presented n-octanesulfonate as ion interaction reagent (IIR) and glycolate [12], or NTA [13] in addition to nitric acid eluent which has been used by silica column impregnated with iminodiacetic acid (IDA; $HN(CH_2COOH)_2$) [14].

As formerly demonstrated, employing REE complexes with NTA in an anion exchange system, resulted in an uncommon order of REEs elution [15] where yttrium was perfectly eluted between neodymium and samarium from its neighboring elements [16]. It is really worth noting that chromatographic techniques are considered superior in separation of Y from other REEs owing to the immense resemblance of their chemical properties [17, 18].

In this paper, a new developed method for the selective and quantitative determination of yttrium after separation from the adjacent element, dysprosium, simultaneously with the individual determination of rare earth elements using DX-500 Ion Chromatograph was proposed. To optimize the studied technique, the influence of some parameters concerning the variation in the oxalic acid / diglycolic acid eluents concentration ratio, its introducing time and gradient flow rate have been fully investigated. The method has then to be validated by comparing the determined values for yttrium and individual rare earth elements with that of a certified reference material so that the method can be applied on two geological samples.

2 EXPERIMENTAL

2.1 Apparatus and Reagents

Dionex Ion Chromatograph (DX-500; Sunnyvale, CA, USA) was used to operate the chromatographic measurement of the ions under study. It is provided with GP40 gradient pump, AD20 absorbance detector and a 50 μ L loop injecting valve. Separator ion-exchange columns; Dionex IonPac CG5A guard column (4.6 \times 50 mm) and IonPac CS5A analytical column (4.6 \times 250 mm), including mixed anion and cation beds with sulfonic acid and alkanol quaternary ammonium functional groups, were used to separate the ions under considerations which were then detected utilizing 4-(2-pyridylazo)resorcinol (PAR) as a post column reagent at 530 nm. Finally, data was collected by Advanced Computer Interface System [19].

NH₄OH solution and HCOOH acid were employed for pH modifications using an Orion type pH meter (USA). Various standard solutions of heavy metals and lanthanides have

been prepared by diluting stock solutions of 1000 ppm (Aldrich and Merck, USA). An injected synthetic solution was prepared containing 5 ppm from each of the following six heavy metals (Fe⁺³, Cu, Ni, Zn, Cd, Mn) and the fifteen lanthanide elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Y, Ho, Er, Tm, Yb and Lu. Nanopure water, with specific resistance of 18.2 mega-ohm.cm (M Ω .cm), was used for the preparation of the eluents and the standard solutions. Pyridine-2,6-dicarboxylic acid (PDCA) and oxalic acid eluents as well as PAR were supplied from Aldrich (USA), Knoch-Light (England) and Merck (USA) respectively.

2.2 Chromatographic Conditions

The chromatographic separation of the study ions has been achieved using different eluents under various elution conditions. The mobile phases employed contained constant concentration of PDCA eluent for separation of the worked six heavy metal ions and diverse oxalic / diglycolic acid eluents concentration ratios for the individual determination of the lanthanide ions. Adjusting the considered eluent pH was set up in buffer solutions enclosing 0.1 M NH₄OH solution and 0.05 M KOH. The mobile phase's flow rates were firstly set at 0.9 and 0.1 mL min⁻¹. Fixed post column reagent (PAR) concentration (0.2 mM) was liquefied in 1 M CH₃COOH and 3 M NH₄OH where its flow rate was kept at 0.5 mL min⁻¹.

2.3 Geology of the samples

Three different geological rock samples collected from various areas along Egypt desert were included in the application step of the study advanced procedure. One of which is from the mineralized lamprophyre dykes of Abu Rusheid area which considered as a reference sample. Additionally two samples; xenotime mineral from Wadi Khuda-Wadi Shut area and phosphate rock from Abu Tartur deposit were taken into consideration. An explanation of the geology of each area was listed below.

Abu Rusheid area is located at south of Eastern Desert, Egypt 50 km southwest of Marsa Alam on the Red Sea coast between longitude 34° 46' to 34° 46' 35" E and latitude

24° 37' 16" to 24° 38' N. From the mineralization point of view, the main rock units of Abu Rusheid area are the cataclastic group and the lamprophyre dykes cutting through it [20].

Wadi Khuda-Wadi Shut area lies in the southern zone of the Eastern Desert along the Red Sea coast. It covers a region of around 800 km² between Latitudes 23° 33' - 23° 50'N and longitudes 35° 05' - 35° 26' E. The Wadi Khuda-Wadi Shut area comprises principally of gneisses-migmatites, ophiolitic serpentinite with talc carbonate rocks and schistose metavolcanics. These rock varieties are intruded by syn to late tectonic diorite, granodiorite, ultramafic-mafic and monzogranite intrusions and dissected by post orogenic veins, dykes and quartz plug [21]. Xenotime is a natural yttrium orthophosphate mineral that usually contains small amounts of other heavy REEs such as Yb, Er and Dy. The mineral is tetragonal, with a hardness of 4-5 and a specific gravity of 4.4-5.1. Xenotime, a major source for heavy rare-earth elements, is recovered as a by-product from the concentration of other heavy minerals such as monazite, zircon, ilmenite and garnet [22].

Abu Tartur deposit is situated in Eastern Sahara, in the New Valley area of the Western Desert of Egypt, 50 km² west of El-Kharga [23]. The deposit prolongs over 100 km² at the south-eastern corner of Abu Tartur plateau. Its middle is at 25° 26' N and 30° 02' E. The highest of the plateau lies somewhere in the range 550 and 560 m above mean sea level. The lowlands and scattered hills of the depression south of the Abu Tartur plateau have a height of around 200-300 m above mean sea level [24]. The phosphate formation is formed of lower and upper phosphorite beds isolated by shales, glauconitic sandstone, carbonate rocks and sandstones.

2.4 Sample Digestion

2.4.1 Preparation of the mineralized lamprophyre dyke and phosphate rock samples

The Abu Rusheid mineralized lamprophyre dyke and phosphate rock samples were firstly

passed through an ashing step for 10 hours at 200 °C to devastate the organic matters stuck within the samples. Following ashing, 1 g of each sample was mixed with a blend of concentrated nitric, hydrofluoric, and perchloric acids in a Teflon beaker and heated till dryness using hot plate. For dissolving purpose, the dried samples were transferred separately in a 50 mL measuring flasks using 1:1 vol ratio of HNO₃ acid and nanopure water solution up to the mark.

2.4.2 Fusion of xenotime concentrate

Tracing the procedure described in reference [25], the following steps are implanted with modification. 0.2 g xenotime concentrate was mixed well with 1g lithium metaborate (LiBO₂) in a platinum crucible with ratio of 1:5 for about 10 minutes. The crucible was then placed in the furnace where its content was transferred to PTFE beaker and heated to about 10 minutes at 700 °C. The PTFE beaker is left to cool after which the molten mixture is transferred to a Pyrex beaker containing about 40 mL of 6N HNO₃ then stirred and heated at 60 °C with hot plate magnetic stirrer for about 1 hour in order to dissolve any remaining residue. Small drops of H₂O₂ were added in order to oxidize all ions in the sample solution. Finally, the resulted solution was transferred with nanopure water into a 50 mL measuring flask, completed to the mark and it was then ready to be measured using the study developed ion chromatographic method [25].

3 RESULTS AND DISCUSSION

As commonly known from literature, separation of rare earth elements depends on the existence of the suitable ligands (H₂L) in the eluents and also on the utilization of separation analytical columns (as CG5A and CS5A) which enclose both cation and anion exchange sites [26]. The separation process is mainly dependent on the formation of LnL₃⁻³ species which resulted from the high stability constants of these ligands with the REEs [27].

In a past work [28], the author has been capable, through utilizing a blend of oxalic and diglycolic acids along with nanopure water as a mixed eluent, to separate the rare earth elements (REEs) (La, Ce, Pr, Nd, Sm, Eu, Gd,

Tb, Dy, Ho, Er, Tm, Yb and Lu) through a gradient elution method Figure (1). This has certainly been done before by introducing PDCA eluent with a concentration of 7 mM at pH 3.95 so as to initially elute the heavy metals (Fe^{+3} , Cu^{+2} , Ni^{+2} , Zn^{+2} , Cd^{+2} , Mn^{+2}), in a way to keep away from any conceivable interference with the lanthanides elution and separation [29, 30]. As indicated from the demonstrated work, Y was coeluted in one peak with Dy, so in the present work, many trials were done to solve the problem of separation of Y from Dy simultaneously with individual separation of the other thirteen RREs, including variation in the oxalic acid / diglycolic acid eluents

concentration ratio, its introducing time and gradient flow rate. Though, in order to investigate such objective, oxalic and diglycolic acid eluents stock solutions of 160 mM concentration each were prepared where their pH solutions were adjusted at 4.04 and 4.32 respectively.

3.1 Mixed Eluent Ratio Variation

In the first trial of optimizing the study method, the run has been initiated with PDCA eluent until a run time of 12 minutes followed by introducing four gradients of the mixed eluent (oxalic acid/ nanopure water/ diglycolic acid) with different ratios at different retention

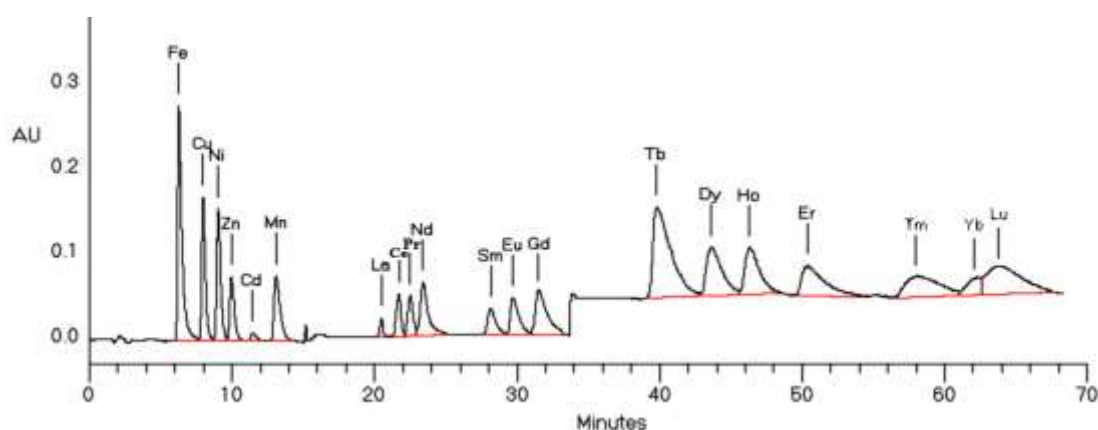


Fig. 1 Chromatogram showing the previously individual separation of the study heavy metal ions and the Rare Earth Elements [28]

Table 1 Eluent run program of the study heavy metals and REE including Y

Eluent (conc. & pH) Run time (min.)	PDCA 7 mM, 3.95 (%)	Oxalic acid 160 mM, 4.04 (%)	Nanopure Water 18.2 MΩ.cm (%)	Diglycolic acid 160 mM, 4.32 (%)
Int.*	Flow rate 0.9 ml/min.			
Int.*	100	-	-	-
0.00	100	-	-	-
12.00	100	-	-	-
12.10	-	40	56	4
18.00	-	40	56	4
18.10	-	40	58	2
24.00	-	40	58	2
24.10	-	40	56	4
31.00	-	40	56	4
31.10	-	26	56	18
33.60	Flow rate 0.1 ml/min.			
69.90	-	26	56	18
70.00	100	-	-	-

*Int.: initial time, mM: milli molar, MΩ.cm: mega-ohm.cm, 1 min. represents 100 units

times and flow rates till the end of the run (Table 1).

By ending the run, it was observed that while the six heavy metals were eluted separately with good resolution, the fifteen lanthanide elements were however eluted in harmonic separated form but with Y overlapped with Dy in one peak (Figure 2). Therefore, it was decided to study the effect of changing the ratio of the gradient program of the used mixed eluents; namely the (oxalic acid / nanopure water / diglycolic acid) for the fourth gradient (26/56/18) respectively. These changes were directed towards decreasing the oxalic acid eluent concentration ratio while increasing that of the diglycolic acid eluent, which is considered the most effective eluent responsible for heavier lanthanides separation.

Many trials were thus performed where the chromatograms shown in Figure (3a,b,c) were obtained under the chromatographic conditions illustrated in Table (2).

As observed from the obtained chromatograms, Dy + Y peak in Figure (3a) has appeared to take a new form towards splitting which by increasing diglycolic acid eluent ratio as in Figure (3b) but with overlap of Tb on Dy + Y peak. Also, Tm, Yb and Lu were appeared to be eluted overlapped in one peak. So, thoughts were directed towards decreasing the diglycolic acid ratio and increasing the oxalic acid ratio as in Figure (3c) but the obtained chromatogram shown undesired results.

3.2 Fourth Gradient Eluent Period Time Variation

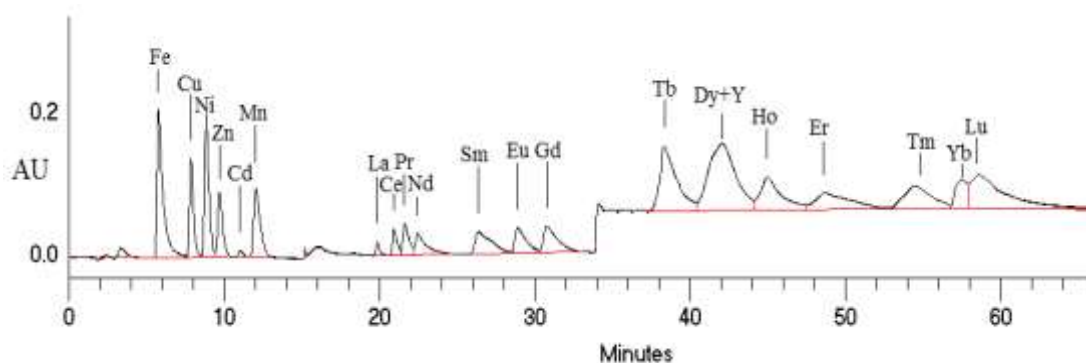


Fig. 2 Chromatogram of the study heavy metal ions and the REEs showing the overlap between Y and Dy

Table 2 Eluent run program showing the effect of mixed eluent ratio variation on Y and REEs individual separation

Eluent (conc. & pH)	PDCA 7 mM, 3.95 (%)	Oxalic acid 160 mM, 4.04 (%)	Nanopure Water 18.2 MΩ.cm (%)	Diglycolic acid 160 mM, 4.32 (%)
Run time (min.)				
Int.*	Flow rate 0.9 ml/min.			
Int.*	100	-	-	-
0.00	100	-	-	-
12.00	100	-	-	-
12.10	-	40	56	4
18.00	-	40	56	4
18.10	-	40	58	2
24.00	-	40	58	2
24.10	-	40	56	4
31.00	-	40	56	4
31.10	-	22/18/30	56	22/26/14
33.60	Flow rate 0.1 ml/min.			
69.90	-	22/18/30	56	22/26/14
70.00	100	-	-	-

*Int.: initial time, mM: milli molar, MΩ.cm: mega-ohm.cm, 1 min. represents 100 units

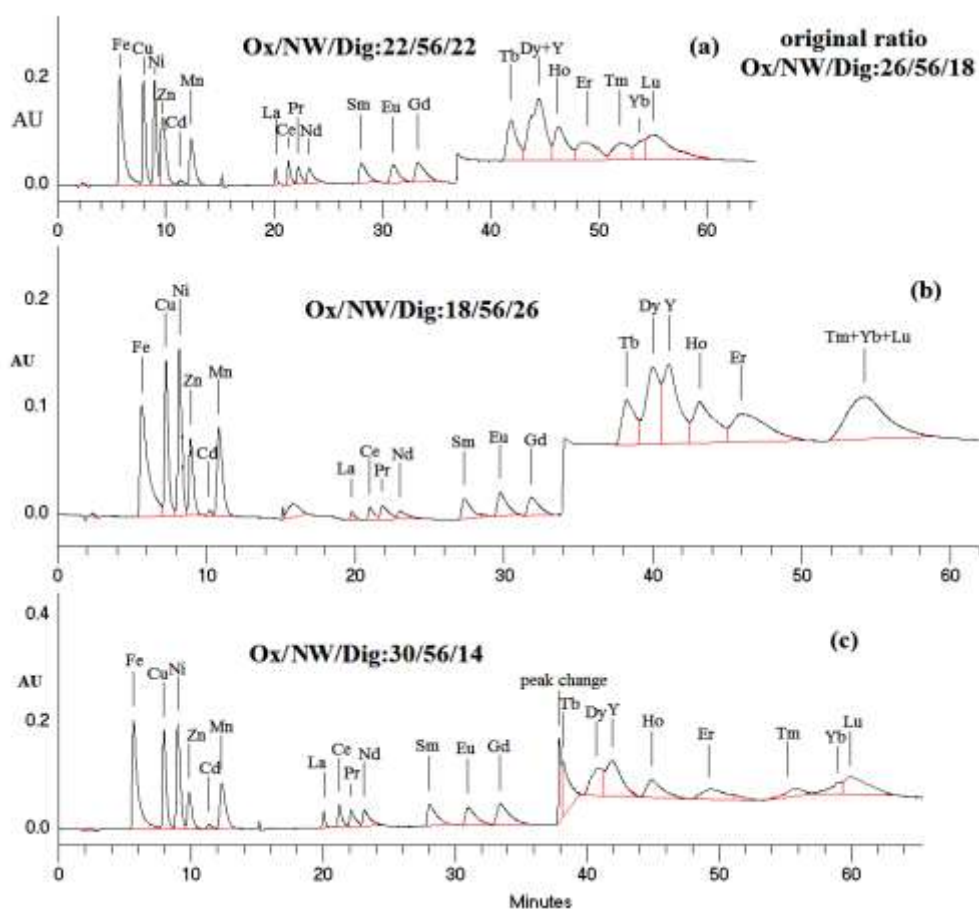


Fig. 3 Chromatogram showing the effect of mixed eluent ratio variation on Y and REEs individual separation

As concluded from the above trials, Y separation from Dy didn't achieved, therefore, the author directed the thought towards changing the fourth gradient eluent period time from 2.5 minutes to 2, 3, and 4 minutes in order increase the effect of the eluent concentration ratio. So modifying the conditions in Table (2), where the fourth gradient eluent ratio (26/56/18) for (oxalic acid / nanopure water / diglycolic acid) respectively was introduced from retention time 31.10 - 33.10 min., from 31.10 - 34.10 min. and from 31.10 - 35.10 min. for 2, 3, 4 minutes period time respectively. The resulted chromatograms were as obtained in Figure 4 (a,b,c).

Investigations from the obtained chromatograms indicated that decreasing the fourth gradient eluent period time as in Figure 4a resulting in overlapping of Gd peak with the peak change in addition to eluting the peaks from Tb - Lu with shifting to higher retention

time without any effect on Dy + Y peak. Increasing the fourth gradient eluent period time to 3 minutes (Figure 4b) couldn't actually attribute any tangible change on Y separation. Further increasing in period time to 4 minutes as observed from Figure 4c resulted in great overlap between the peaks from Tb - Lu where Tb peak eluted in a manner overlapped with the change peak as also appeared between Tm, Yb and Lu. Dy + Y peaks showed small splitting.

3.3 Fourth Gradient Eluent and 0.1 ml/min Flow Rate Introducing Time Change

By reviewing the above studied variation factors and after some unsuccessful trials, it can be pointed out that Y peak didn't separated from Dy peak either by variation of the mixed eluent ratio or fourth gradient eluent period time. So, in order to realize an improvement in the separation of the Y peak from the collective peak Dy + Y, the author targeted her thought, in the next trial, to return to the starting

conditions in Table (1) and to change the introducing time of both of the fourth gradient mixed eluent (from 31.10 to be 24.10 min.) and 0.1 ml/min. flow rate (from 33.60 to be 26.10 min.) deleting the third gradient eluent (40/56/4) for (oxalic acid / nanopure water / diglycolic acid) respectively to be as illustrated in Table (3). The resulted chromatogram was as shown in Figure (5).

From the obtained chromatogram (Figure 5), it was resulted that “Y” peak was separately eluted in a better manner than that in the selected chromatogram of Figure (2) where the collective peak (Dy + Y) was clearly splitted into Dy and Y peaks with retention times 48.87 and 50.57 min. respectively but with some overlap between them as between Y and Ho. Also an overlap was observed between Eu and Gd peaks. Other elements have been eluted in good separation behavior.

3.4 Third Gradient Eluent Ratio Variation

In a trial to achieve more separation between Dy, Y and Ho peaks as well as between Eu and Gd, the author tried to vary the ratio between the gradient of the third mixed eluent (26/56/18) for (oxalic acid / nanopure water / diglycolic acid) respectively as represented in Table (4). It was observed from the corresponding chromatograms that increasing the diglycolic acid ratio (22%) and decreasing that of the oxalic acid (22%) as in Figure (6a) resulted in eluting Dy and Y completely overlapped in one peak with Tb and Ho appearing overlapped to (Dy+Y) peak but with much more extent for Ho. Yb and Lu achieve more separation while Eu and Gd eluted without any change in their behavior.

Table 3 Eluent run program showing the effect of changing both the introducing time of the fourth gradient eluent and 0.1 ml/min. flow rate on Y and REEs individual separation

Eluent Run time (min.)	PDCA 7 mM, 3.95 (%)	Oxalic acid 160 mM, 4.04 (%)	Nanopure Water 18.2 MΩ.cm (%)	Diglycolic acid 160 mM, 4.32 (%)
Int.*	Flow rate 0.9 ml/min			
Int.*	100	-	-	-
0.00	100	-	-	-
12.00	100	-	-	-
12.10	-	40	56	4
18.00	-	40	56	4
18.10	-	40	58	2
24.00	-	40	58	2
24.10	-	26	56	18
26.10	-	26	56	18
26.20	Flow rate 0.1 ml/min.			
69.90	-	26	56	18
70.00	100	-	-	-

*Int.: initial time, mM: milli molar, MΩ.cm: mega-ohm.cm, 1 min. represents 100 units

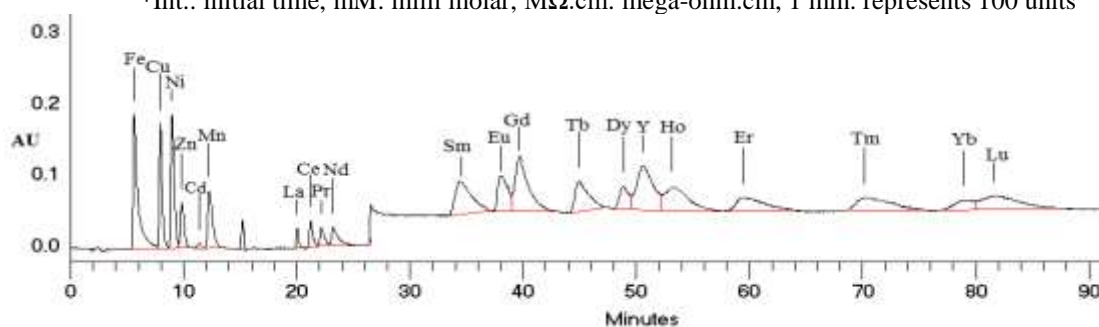


Fig. 5 Chromatogram showing the effect of changing the introducing time of both of the fourth gradient eluent as well as 0.1 ml/min. flow rate on Y and REEs individual separation

Table 4 Eluent run program showing the effect of third gradient eluent ratio variation on Y and REEs individual separation

Eluent (conc. & pH) Run time (min.)	PDCA 7 mM, 3.95 (%)	Oxalic acid 160 mM, 4.04 (%)	Nanopure Water 18.2 MΩ.cm (%)	Diglycolic acid 160 mM, 4.32 (%)
Int.*	Flow rate 0.9 ml/min			
Int.*	100	-	-	-
0.00	100	-	-	-
12.00	100	-	-	-
12.10	-	40	56	4
18.00	-	40	56	4
18.10	-	40	58	2
24.00	-	40	58	2
24.10	-	22/29/32/34	56	22/15/12/10
26.10	-	22/29/32/34	56	22/15/12/10
26.20	Flow rate 0.1 ml/min.			
99.90	-	22/29/32/34	56	22/15/12/10
100.00	100	-	-	-

*Int.: initial time, mM: milli molar, MΩ.cm: mega-ohm.cm, 1 min. represents 100 units

Trying to go in the opposite direction i.e. increasing the oxalic acid eluent ratio (29%) and decreasing that of the diglycolic acid (15%) (Figure 6b), created good separation between all the peaks either between Eu and Gd or between Dy, Y and Ho in addition to complete separation of Tb peak but Yb and Lu peaks are not eluted. Completing the in the same direction, chromatogram (6c) appeared significant separation for all the peaks including Eu, Gd, Tb, Dy, Y, Ho but the run ended without eluting Er, Yb and Lu due to eluting all the worked peaks with shifting to higher retention time. Going through more increasing in oxalic acid eluent ratio with decreasing of that of the diglycolic acid (Figure 6d) appeared good separation for Eu, Gd and Tb but great overlap took place again between Dy, Y and Ho.

From the resulted trials concerning variation in the eluents ratio in the third gradient, it can be concluded that the best obtained chromatogram is that shown in Figure (6c). So, it was decided to take its conditions and complete the elution of Er, Yb and Lu which necessitates the introduction of new eluent gradient (fourth gradient in that case) with higher concentration ratio for both the

oxalic and diglycolic acid eluents than the third gradient eluent for the selected conditions.

3.5 New Fourth Gradient Eluent Introducing Time Variation

New fourth gradient eluent ratio is decided to be introduced to the selected chromatogram (Figure 6c) conditions with higher concentration ratio to be (22/56/22) for (oxalic acid / nanopure water / diglycolic acid) respectively with different introducing times at 45, 52 and 55 minutes. Under these conditions the obtained chromatograms indicated that these working conditions have been able to successfully separate all the worked peaks in a manner better than that in Figure (6c) but with some overlap between Y and Ho. Best chromatogram obtained from these conditions is shown in Figure (7) and its conditions are represented in Table (5).

3.6 The Fourth Gradient Eluent Ratio Change

Trying to realize a better separation for all the peaks especially between Y and Ho, another trial was performed in which the ratio of the applied fourth gradient eluents was changed to 26%/56%/18% for the oxalic acid eluent/nanopure water/diglycolic acid eluent

respectively i.e. decreasing the latter at the

So in this way, by identifying all the

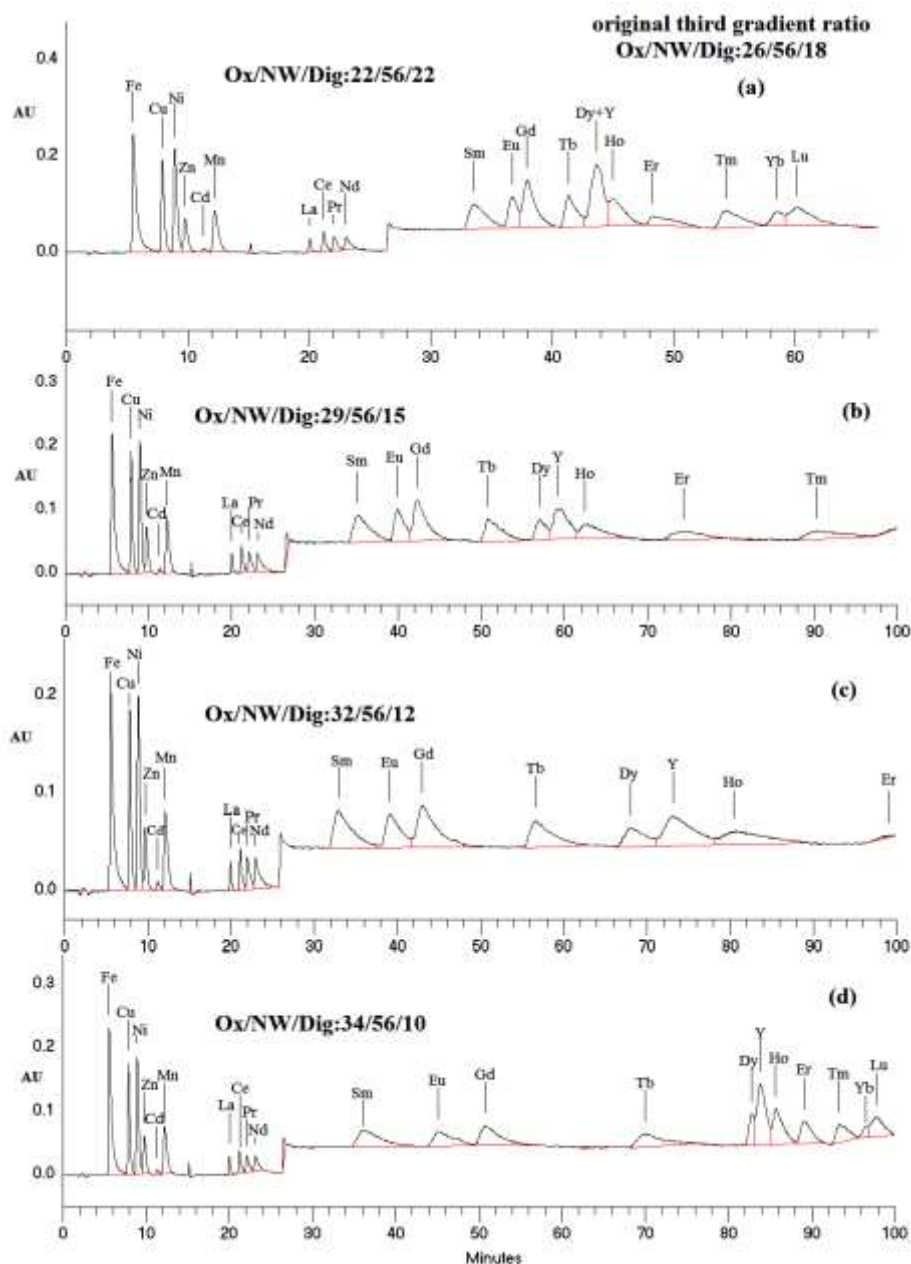


Fig. 6 Chromatogram showing the effect of third gradient eluent ratio variation on Y and REEs individual separation

expense of the former (Table 6). From the obtained corresponding chromatogram shown in Figure (8), it was revealed that changing the fourth gradient eluent ratio has actually attained a high degree of perfection where it has expressed an adequately excellent separation for all lanthanide elements from (La - Lu) including Y as well as the studied heavy metals.

separated peaks expressed in Figure (8), the author had accomplished the point of the current research where the final optimized chromatogram conditions were represented in Table (6).

3.7 Calibration of the Optimized Study Method

After achieving optimization of the developed ion chromatographic method, calibration was occurred using various standard

solutions of the study heavy metal ions ranging from 1-10 ppm as well as for the lanthanides (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb) whereas for the other heavy lanthanides (Dy, Y, Ho, Er, Tm, Yb, Lu), concentrations from 1-6.3 ppm were prepared. As presented from the data given in Table (7), good linear relations with high correlation coefficients have been observed for each element.

3.8 Validation, Application and Performance of the Optimized Study Method

In the wake of improving the studied ion chromatographic method for the individual determination of some heavy metals and Y

simultaneously with the other fourteen rare earth elements as presented in Figure (8), consequently, validation and application of the considered optimized conditions (Table 6) upon three Egyptian geological materials has been occurred. These study geological materials have included three samples; the first one is signified as a reference sample gathered from the mineralized lamprophyre dykes of Abu Rusheid area (South Eastern Desert of Egypt) and has been analyzed by the ACME Analytical Laboratories Limited, Vancouver, Canada by ICP-MS (Agilent 7900) technique. The second sample is xenotime mineral from Wadi Khuda-Wadi Shut area (South Eastern

Table 5 Eluent run program showing the effect of introducing the new fourth gradient eluent at 55 minute in run time on Y and REEs individual separation

Eluent Run time (min.)	(conc. & pH)	PDCA 7 mM, 3.95 (%)	Oxalic acid 160 mM, 4.04 (%)	Nanopure Water 18.2 MΩ.cm (%)	Diglycolic acid 160 mM, 4.32 (%)
Int.*		Flow rate 0.9 ml/min			
Int.*		100	-	-	-
0.00		100	-	-	-
12.00		100	-	-	-
12.10		-	40	56	4
18.00		-	40	56	4
18.10		-	40	58	2
24.00		-	40	58	2
24.10		-	32	56	12
26.10		-	32	56	12
26.20		Flow rate 0.1 ml/min.			
55.10		-	32	56	12
55.20		-	22	56	22
99.90		-	22	56	22
100.00		100	-	-	-

*Int.: initial time, mM: milli molar, MΩ.cm: mega-ohm.cm, 1 min. represents 100 units

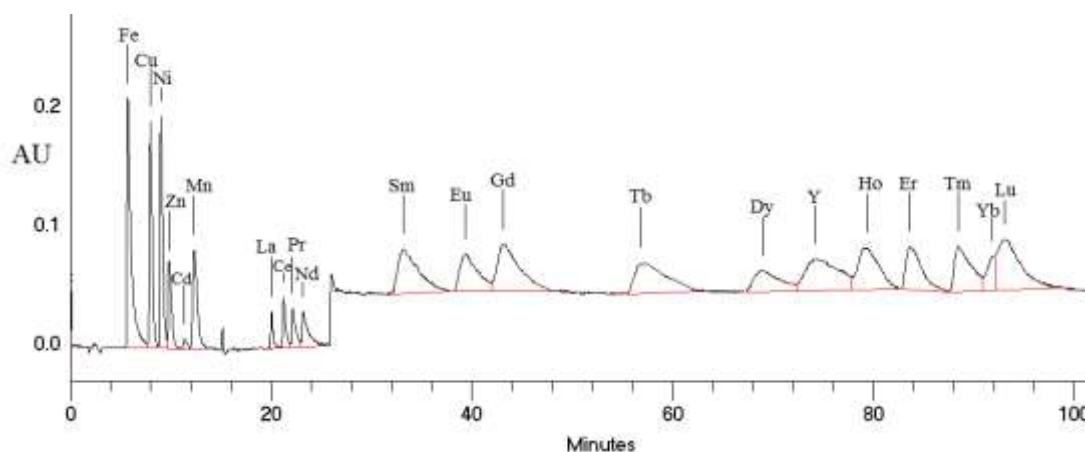


Fig. 7 Chromatogram showing the effect of introducing the new fourth gradient eluent at 55 minute in run time on Y and REEs individual separation

Table 6 Eluent run program showing the effect of changing the fourth gradient eluent ratio to (26/56/18) for (oxalic acid / nanopure water / diglycolic acid) respectively on Y and REEs individual separation (optimum run program conditions for the developed method)

Eluent (conc. & pH) Run time (min.)	PDCA 7 mM, 3.95 (%)	Oxalic acid 160 mM, 4.04 (%)	Nanopure Water 18.2 MΩ.cm (%)	Diglycolic acid 160 mM, 4.32 (%)
Int.*	Flow rate 0.9 ml/min			
Int.*	100	-	-	-
0.00	100	-	-	-
12.00	100	-	-	-
12.10	-	40	56	4
18.00	-	40	56	4
18.10	-	40	58	2
24.00	-	40	58	2
24.10	-	32	56	12
26.10	-	32	56	12
26.20	Flow rate 0.1 ml/min.			
55.10	-	32	56	12
55.20	-	26	56	18
119.90	-	26	56	18
120.00	100	-	-	-

*Int.: initial time, mM: milli molar, MΩ.cm: mega-ohm.cm, 1 min. represents 100 units

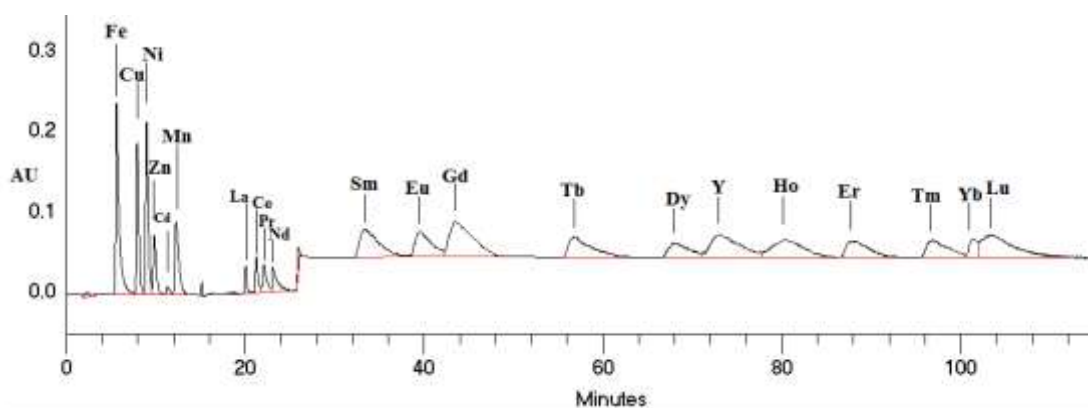


Fig. 8 Chromatogram showing the effect of changing the fourth gradient eluent ratio to (26/56/18) for (oxalic acid / nanopure water / diglycolic acid) respectively on Y and REEs individual separation (optimum chromatogram for the developed method)

Table 7 Correlation coefficients values of the studied heavy metal ions and the rare earth elements

Heavy Metals Ions	Correlation Coefficients (R ²)	Rare Earth Elements	Correlation Coefficients (R ²)	Rare Earth Elements	Correlation Coefficients (R ²)
Fe ⁺³	0.9986	La	0.9904	Dy	0.9988
Cu	0.9997	Ce	0.9918	Y	0.9959
Ni	0.9966	Pr	0.9942	Ho	0.9945
Zn	0.9968	Nd	0.9957	Er	0.9929
Cd	0.9998	Sm	0.9987	Tm	0.9931
Mn	0.9997	Eu	0.9992	Yb	0.9933
		Gd	0.9979	Lu	0.9959
		Tb	0.9971		

Desert of Egypt) whereas the third one represents a sample from Abu Tartour phosphate deposits (Western Desert of Egypt).

The results obtained from the comparison of the reference Abu Rusheid sample which was analyzed by both ACME Lab. using ICP-MS and the currently developed ion chromatographic method has been demonstrated in Table (8). It is obviously apparent that there is a nearly good agreement between the two procedures.

Table 8 Comparison of the analyzed results of the Abu Rusheid lamprophyre dykes sample for the individual determination of the heavy metal ions, Y and the REEs.

Elements	ACME Lab. ICP-MS (ppm)	IC Procedure (ppm)	RSD* (%)
Heavy Metals	N.A.	5.49%	± 0.051
Fe	350.7	340.7	± 0.022
Cu	6.40	5.90	± 0.043
Ni	6876	6865.1	± 0.015
Zn	11.60	10.77	± 0.034
Cd	N.A.	1561.2	± 0.027
Mn			
REE			
La	172.9	160.3	±0.048
Ce	168.7	164.8	±0.015
Pr	119.2	115.8	±0.032
Nd	432.7	426.8	±0.024
Sm	169.1	165.2	±0.051
Eu	6.00	5.20	±0.022
Gd	223.8	221.5	±0.045
Tb	43.43	40.21	±0.031
Dy	532.4	533.6	±0.017
Y	4077	4074.8	± 0.026
Ho	152.6	149.7	± 0.014
Er	734.7	730.2	± 0.033
Tm	141.8	138.3	± 0.043
Yb	1268.2	1260.7	± 0.027
Lu	157.30	151.9	± 0.041

where; N.A.: Not Analyzed, *: Employing 3 injections in 3 independent runs

The study advanced ion chromatographic method was then additionally applied for the individual determination of some heavy metals, Y and the other fourteen rare earth elements on the two considered samples (xenotime mineral and Abu Tartur phosphate rock) as investigated in Table (9).

Table 9 Analyzed results of xenotime and Abu Tartur phosphate rock samples for the individual determination of the heavy metal ions, Y and the REEs.

Elements	Xenotime Sample (ppm)	RSD* (%)	Phosphate Rock Sample (ppm)	RSD* (%)
Heavy Metals	55000	± 0.055	3.11 %	± 0.030
Fe	17.20	± 0.027	10.13	± 0.014
Cu	8.60	± 0.015	21.45	± 0.026
Ni	139.10	± 0.023	132.75	± 0.042
Zn	15.60	± 0.033	4.10	± 0.019
Cd	1123.41	± 0.041	1003.3	± 0.031
Mn				
REE	(%)			
La	0.512	± 0.015	162.65	± 0.032
Ce	2.360	± 0.034	310.20	± 0.012
Pr	0.088	± 0.019	153.11	± 0.042
Nd	1.457	± 0.043	177.00	± 0.016
Sm	0.862	± 0.023	34.00	± 0.027
Eu	0.086	± 0.035	7.30	± 0.022
Gd	2.125	± 0.027	39.00	± 0.017
Tb	0.255	± 0.014	4.30	± 0.030
Dy	3.833	± 0.022	36.90	± 0.041
Y	22.722	± 0.017	273.3	± 0.025
Ho	1.091	± 0.041	32.15	± 0.036
Er	2.361	± 0.012	3.90	± 0.021
Tm	0.744	± 0.025	2.72	± 0.042
Yb	2.546	± 0.033	15.10	± 0.017
Lu	0.736	± 0.027	1.20	± 0.033

*: Employing 3 injections in 3 independent runs

Performance of the currently advanced ion chromatographic method been evaluated by determining the relative standard deviation (RSD) values for the study heavy metal ions and the lanthanide elements of the three working geological samples (Tables 7, 8) where each sample was injected for three independent runs. Number of sample injections, element mean values and element standard deviation values were determined and taken in consideration for calculating RSD values.

CONCLUSION

A new chromatography procedure had been advanced for yttrium separation from dysprosium simultaneously with individual determination of rare earth elements. The method had included a unique separation system of the fifteen lanthanide elements including Y preceded by six heavy metal ions under optimization conditions of eluent's concentration and flow rate. The results obtained from the three applied geological samples acquired very low RSD percentages. The progressed method permits direct injection

of the samples without pre-complexation and further manipulation of analytes.

Disclosure statement

The author declares that they have no conflict of interest.

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التقدير الكروماتوجرافي الأيوني للإيتريوم بعد الفصل من الديسبروسيوم بالتزامن مع التقدير الكمي الفردي للعناصر الأرضية النادرة

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ملخص

تم تطوير طريقة كروماتوجرافية أيونية معينة لتقدير الإيتريوم بعد الفصل من الديسبروسيوم بالتزامن مع التقدير الكمي الفردي للعناصر الأرضية النادرة. تم تحقيق الفصل الانتقائي للإيتريوم من الديسبروسيوم بالإضافة إلى العناصر الأرضية النادرة الثلاثة عشر الأخرى عن طريق الإزاحة المتدرجة باستخدام خليط حمض الأوكساليك / حمض ثنائي الجليكوليك على عمود فصل IonPac CS5A بعد ذلك تم الكشف عن الأيونات المنفصلة باستخدام 4-(2-بيريديل أزو)ريسرسينول (بار) عند 530 نانومتر. تم التحقق من صحة الطريقة المثلى بعد ذلك عن طريق تحليل عينة مرجعية من منطقة أبو رشيد تلاها تطبيقها على مادتين جيولوجيتين من منطقة وادي خودة - وادي شوت ورواسب فوسفات أبو طرطور. تم التعبير عن الانحراف المعياري النسبي (RSD) المحسوب للعينات التي تم تحليلها بقيم منخفضة للغاية الأمر الذي يؤكد إكهام الطريقة المطورة. أتاح العمل الحالي التقدير الفردي لعناصر اللانثينيدات بما في ذلك Y وستة أيونات معدنية ثقيلة في وقت مطلق يبلغ حوالي 110 دقيقة.