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Distribution of REE in shales overlying the Abu Tartur phosphorite deposit, Western Desert, Egypt

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Abstract

The phosphorite deposit of Abu-Tartur plateau, Western Desert, Egypt is one of the largest phosphorite deposits of the world. Previous investigations had revealed that these deposits contain appreciable amounts of rare earth elements (REE) reaching up to 2000 ppm. The distribution pattern of REE indicate terrestrial origin, whereas the phosphorites are of marine origin. This situation suggests that the REE have been remobilized and incorporated into the phosphorites postdepositionally. For this reason it was found of interest to investigate the REE distribution within the overlying shales and their association with different minerals. Samples from the phosphorites and overlying shales have been provided by the Geological Survey and Mining Authority, Egypt. Both ICP–AES and ICP–MS techniques were used for the quantitative determination of the individual REE. Normalized distribution patterns prove that REE in both phosphorites and shales are of terrestrial origin. The vertical distribution of REE in *m*% within the overlying shales and the abnormally high concentrations of REE in this formation relative to their normal background values in addition to the association of REE with aluminum silicate minerals and not with apatite (which is found in very low concentrations) all suggest that the provenance of REE is the overlying shales. More detailed studies have to be carried out to verify this finding. © 1998 Elsevier Science S.A.

Keywords: Phosphorites; Shales; Rare earth elements

1. Introduction

Preliminary investigations on the abundance and distribution patterns of REE in Abu-Tartur phosphorites have been carried out previously by researchers on a limited number of samples [1–4]. One of the objectives of investigating the REE abundance in phosphorite deposits in general is the possibility of their extraction as by-products during phosphoric acid and fertilizer manufacture.

Due to the fact that the physico-chemical environment conditions do not allow the REE to be fractionated easily during sedimentation, the REE distribution patterns could provide some clues elucidating the average composition of their provenance [5]. Since the REE are transported either in particulate matter or in solution i.e. the process of remobilization, the average sedimentary REE pattern of phosphorites is equated to the average shale REE pattern. The North American Shale Composite (NASC), [6] has been in use for normalizing REE since 1968 [7]. McArthur and Walsh, [8], have suggested that, the bulk of the REE in most phosphorite deposits is incorporated post-depositionally during the slow and continuous course of diagenesis and catagenesis. They classified the REE distribution patterns into four types on the basis of their provenance: the 'shale' type; the 'sea water' type; the 'weathered' type and finally the 'mixed' type, the patterns of which do not follow any of the three previous ones.

The question of REE mobilization and incorporation from one lithological facies into another during diagenesis is still not yet well understood. Several researchers have contributed to elucidate the mechanism of this process [9–17]. Most of these investigators point out that the use of REE as indicators for sediment provenance should be treated with extreme caution since significant REE migration and possible fractionation is expected to have occurred during their diagenesis. Kolodny, [14], in his review on marine phosphorites states that the REE may be entering the apatite lattice not only upon its formation but also during post-depositional changes. He argues that if this is true for submarine phosphorites, one cannot exclude the possibility that REE enrichment in the on-land phosphorites is also the result of late epigenetic emplacement of these elements into the lattice.

Milodowski et al. [17], in their study on the REE redistribution during diagenesis of a turbidite/hemipelagite mudrock sequences of Llandovery in Central Wales have

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adopted an approach to account for REE possible diagenetic changes. They chose one of the localities with REE abundances assuming it represents the pre-diagenetic muddy sediment of the region and applied it as a reference to account for diagenetic changes in other associated units. They concluded that the localized REE redistribution between adjacent lithologies is similar to that reported by Schieber, [16], from shale–limestone sequences in the Newland formation, Montana. Nesbit [12] has proposed a model to account for the remobilization of REE within a section of fresh granodiorite, variably weathered granodiorite and residual clay material. He notes that although REE are mobilized during weathering under the effect of aggressive CO_2 and organic acid-charged rainwater, they are primarily recycled within the weathering profile rather than transported significant distances in solution. For sedimentary studies the importance of Nesbitt's work is that it supports suggestion that for the most common weathering conditions, REE are dominantly transported from the weathering profile by mechanical processes.

Condie [18], in his study to elucidate which minerals host the REE in shales and how they are actually transferred from source to suspended load in rivers to fine-grained marine sediments which after lithification can become shales, has concluded that REE correlates positively with $Al_2\ O_3$ ($R=0.7$), suggesting that clays are important in hosting REE. On the contrary he found no correlation between REE and P_2O_5 content. This indicates that apatite does not typically control REE distribution in shales.

The aim of the present investigation is to elucidate the Abu-Tartur phosphorite REE source, their distribution within the commertial phosphorite bed and the overlying shales and establish geochemical relationships and parameters characteristic of this deposit for any future exploratory activities over this phosphorite deposit.

2. Geological setting of the deposit

The Abu-Tartur phosphorite deposit is situated in the south-western sector of Egypt in the Western Desert. The deposit is part of a vast phosphorite-bearing region comprising the Dakhla and Kharga oases (and the Abu-Tartur plateau in between) and extending for more than 200 km latitudinally and 150 km meridionally. Stratigraphically the deposit is composed of a variety of sedimentary rocks ranging from pre-Maestrichtian to Quaternary [19]. The phosphorite formation can be divided into three lithological members (from base to top): the phosphorite member (the pelletal commertial phosphorite ore with average P_2O_5 content of 25.9%); the glauconite-carbonate-sandy-clay member overlies conformably the preceeding one; and the topmost member of mixed gravel phosporite and carbonate shales. The phosphorite-bearing and enclosing rocks of Abu-Tartur plateau represent platform sediments that are confined to an old (apparently pre-Cambrian) bay-like tectonic depression enclosed between the Dakhla and Kharga old uplifts. Structurally they form a large gentle syncline. The phosphorite ore is mainly composed of flour-apatite; dolomite and calcite (3–15%) as cementing material to the phosphate; gypsum and marcasite (3–4.5%); hematite and limonite (1–2%); clay minerals (2.5–5%) and organic carbon (0.1–0.3%).

Due to the fact that the phosphorites occur at depths ranging from 140 to 210m below the surface of the plateau, drilling was adopted as the main exploratory technique. Over 100 boreholes were drilled by the Geological Survey of Egypt (GSE). The average core recovery of the phosphorite bed was 83.3%. Gamma logging was carried out by the GSE for the verification of the phosphorite bed thickness, depth of the core samples and investigation of their structure ([19]). The material for the present study is provided by the GSE and is selected from a number of boreholes covering an area of about 17 km^2. The grid pattern adopted by the GSE for exploratory borehole drilling is 400×400m. and represented by the coordinates 52–18/G–N.

The core samples were collected by splitting the core along its long axis into two equal parts, one of which was entirely included into the sample and the other half was kept as a duplicate. Representative samples were taken from the latter for petrographic and other physico-mechanical studies, the results of which were previously reported by the GSE [19].

The shale samples from the phosphate overlying shale formation have been collected along three vertical sections. The thickness of the shale varies from 20–60 m. and is composed predominantly of shales, dark grey calcareous-clayey mudstone, calcareous shales with pelecypod shells. Some thin (10–15 cm) intercalations of fine concretional phosphorites and weakly phosphatized carbonate rocks are recorded also.

3. Analytical procedure

The quantitative determination of REE has been one of the difficult tasks for spectroscopists and analytical chemists. The advances over the past two decades in the field of inductively coupled plasma spectrometry in general and in ICP–MS in particular, furnish the basis for adopting fast, sensitive and reliable physical techniques for the elemental analysis of geological material [20]. ICP–MS together with ICP–AES [21–25] have been adopted in the present investigation for the analysis of REE, Y and Sc.

Approximately 50 mg of powdered sample was weighed into a teflon dissolution container (Savillex), and dissolved in HF and $HClO_4$. After dissolution, samples were dried and then redissolved with 6 N HCl. Two standard reference materials were used for data validation. The first is

NIST-694 phosphate rock for low REE concentrations, and the second is an apatite-nepheline syenite sample provided by the REE Institute in Moscow for high REE concentrations. The phosphorite core samples and the shale composite ones were analyzed for REE, Y and Sc using a Finnigan SOLA ICP–MS at the Department of Geosciences, University of Arizona and using an ICP–AES technique developed at the spectroscopy department, NRC, Egypt [25]. The other Chemical data (e.g. P_2O_5, Ca O, insoluble residue, total iron) were provided by the GSE. The errors of the analyses based on multiple runs of the standards are $<5\%$ for all REE, except Tm which sometimes reaches 8%.

4. Results and discussion

4.1. REE distribution patterns

The results of REE analyses for a number of representative phosphorite and shale samples are given in Table 1. A representative REE shale (NASC) normalized abundance diagram for samples from the phosphorite bed selected from one borehole is given in Fig. 1.

They all exhibit the 'shale' pattern without Ce negative anomaly. This confirms the assumption that the Abu-Tartur marine phosphorites have incorporated their REE content post-depositionally during a late epigenetic stage of transformation. McArthur and Walsh, [8], have drawn a number of observations regarding the connection between the type of phosphorite, location and age. The older the phosphorite deposit the higher their REE content. Our data are found to be in good agreement with their findings where the abundance of REE in Abu-Tartur phosphorites relative to shale is 5 which is comparable to those values recorded for U.S.A. Phosphoria Formation.

4.2. Origin of REE in phosphorites

The absence of Ce negative anomaly in the REE shale normalized diagrams, suggests that REE were remobilized and incorporated into the phosphorites from the associated shales and clastic debris through diagenesis and catagenesis. The stratigraphic succession of the deposit is composed of a variety of sedimentary rocks ranging from pre-Maestrichtian to Quaternary. From the top to the bottom, it is classified under the following units, (Table 2). The shales of the Dakhla formation (average thickness 60

Table 1
REE (ppm) for shale composite samples from Sector 1 (Dakhla Shale)

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	Sc	Thick. m
1/1	26.7	34.1	3.9	11.5	2.15	0.75	2.1	0.46	1.6	0.35	1.22	0.15	1.3	0.21	4.5	7.2	0.5
1/2	26.3	52	6.4	25	6.7	2.55	8.4	2.3	13.2	2.9	9.87	1.46	9.5	1.4	78.4	7.6	1.1
1/3	78.2	106	16	60.5	14.8	4.9	16.6	3.76	17.8	3.9	10.6	2.5	8.3	2.6	78.2	5.4	0.3
1/4	25.4	40	5	17.4	4.7	1.1	2.5	0.64	2.4	0.42	1.3	0.2	1.3	0.36	4.96	7.9	0.4
1/5	11.1	22.5	2.7	10.2	2.4	0.73	2.2	0.47	1.57	0.36	1.18	0.15	1	0.28	5.9	2.6	0.45
1/6	22.8	35.4	3.7	11.2	3.4	0.95	2.8	0.55	1.97	0.4	1.2	0.2	1.5	0.37	6.27	5.9	4
1/7	18.4	37.5	4.5	16.3	3.8	1.3	4.5	0.65	3.4	0.74	1.9	0.33	1.2	0.43	9.04	5.8	0.5
1/8	20.5	34.4	3.6	11.8	2.6	0.74	2.6	0.52	1.8	0.42	1.16	0.14	1.7	0.28	6.4	8.5	2.5
1/9	57.3	96	11	45.3	9.3	2.4	9.26	1.97	8.6	1.85	5.5	0.73	5.3	0.78	60.3	4.3	0.25
1/10	45.5	83.4	8	26.9	5.9	1.89	5.3	1.16	4.7	0.98	3.56	0.33	2.7	0.44	20.9	4.8	3.4
1/11	35	45.1	3.5	12.3	4.5	1.1	4.2	0.74	3.4	0.68	2.2	0.27	1.7	0.34	11.4	5.4	0.7
1/12	9.3	15.6	2.2	10.5	2.3	1.05	3	0.53	3.6	0.58	1.9	0.26	2.3	0.69	8.9	3.6	1.1
1/13	66.1	161	21.5	102	32.9	9	32.2	6.2	35	6.4	19.3	2.2	14.3	2.16	162	9.2	1.3
1/14	67.5	115	12.2	50.2	10	2.8	11.2	2.34	11.5	2.33	7.77	0.97	6.1	5.94	83.5	7.2	0.4
1/15	40.7	85.5	10.8	46	8.5	2.7	10.7	2	9.6	2.05	6.03	0.68	5.4	0.62	48.7	8.5	1
1/16	76.7	167	17.9	72.1	15.2	4.1	15.8	3.2	12.7	2.62	8.63	0.97	6.8	1.1	55.4	8.7	0.6
1/17	16.7	33	3.1	10.4	2.6	0.97	2.3	0.4	1.9	0.4	1.41	0.24	1.7	0.29	3.9	9.5	0.5
1/18	9	14.3	1.78	6.23	1.27	0.9	2.4	0.68	2.4	0.5	1.5	0.28	1.1	0.4	4.5	3.6	1.7
1/16’	179	380	47.3	175	37.6	9.6	37.8	7.2	30.2	5.9	20.2	2.1	15	2.1	162	12	0.6
1.17’	18.1	30	3.56	10.8	1.68	0.9	2.5	0.64	2.4	0.35	1.1	0.26	1.4	0.3	3.5	8.9	0.5
1/18’	12.3	12.2	1.77	6.79	2.06	1.1	2.2	0.61	1.15	0.57	0.73	0.29	1.42	0.43	4.9	3.6	1.7

REE (ppm) for core samples from phosphorite bed

Sample	La	Ce	Nd	Sm	Eu	Gd	Tb	Ho	Er	Tm	Yb	Lu	Y	Sc
J 28/160	62	108	48	10	2.7	13.5	2.0	2.5	6.5	0.8	5.5	0.8	70	13.5
J 28/161	32	68	28	5	1.5	5.5	0.8	0.8	2.5	1.6	2.3	0.4	30	16.5
J 28/162	153	297	142	30	9.0	40.0	5.0	6.5	19.0	2.5	17.0	2.5	230	28.0
J 28/163	220	410	201	41	11.0	55.0	7.2	8.5	25.0	3.5	22.0	3.5	275	34.0
J 28/164	204	385	180	37	10.0	50.0	6.5	8.0	23.0	3.1	20.0	3.1	256	32.0
K 32/192	208	515	146	25	8.0	31.0	6.0	10.0	22.0	4.6	48.0	3.5	133	13.0
K 32/194	174	203	160	33	9.0	42.0	5.5	7.0	21.0	2.7	17.7	2.7	277	27.0
K 32/195	200	395	200	41	11.0	54.0	6.9	8.5	25.0	3.4	22.0	3.4	346	33.0

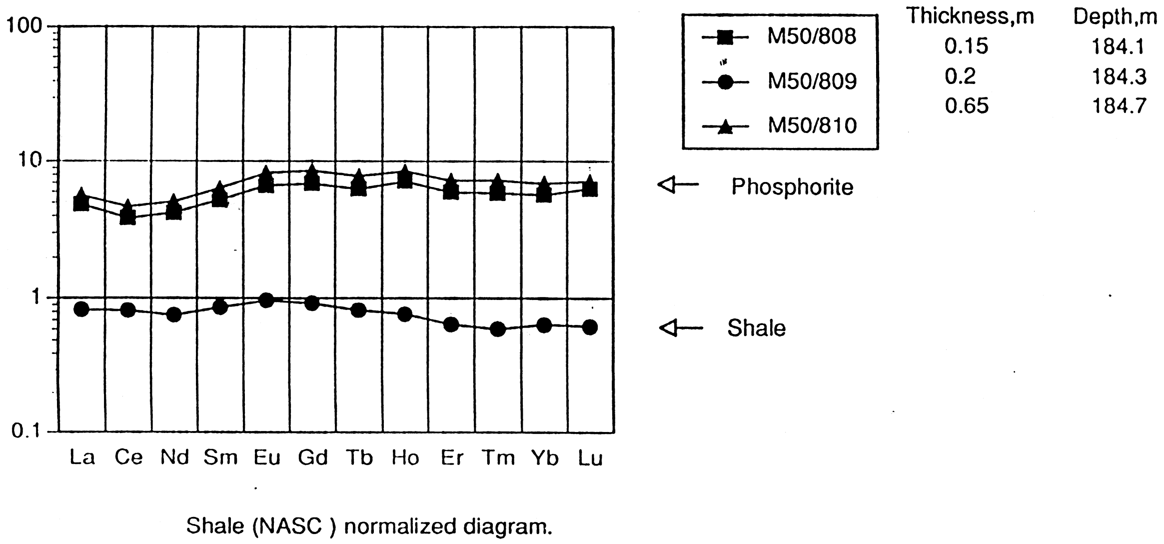

Fig. 1. Shale (NASC) normalized diagram.

m) are characterized by a uniform mineralogical composition and structure. Three bio-stratigraphic units are distinguished among this formation (from bottom to top), [19]:-

1. The member of shales, 22–44 m thick, predominately shales, calcareous shales and mudstone with pelecypod shells.
2. The member of carbonate shales; 22–27 m thick, alternating carbonate shales with carbonate intercalations with phosphate concretions and abundant pelecypod shells.
3. The phosphate-shale member, 34–45 m thick, shales with thin intercalations of fine concretional phosphorites.

It is most probable that the source of REE in the Abu-Tartur phosphorites is the shales of the phosphate formation (Fig. 1) as well as those of the Dakhla formation. Table 1 and Fig. 2 illustrate the variations in individual and total REE within the Dakhla shale formation. The fact that some samples have high REE content (e.g. over 600 ppm, 1/16) and at the same time having a P_2O_5 content less than 3%, favours the assumption that the REE in the shales were initially highly enriched and were not associated with phosphates (no positive correlation between REE and P_2O_5) [18]. Most probably the REE in the shales were initially present with the clay minerals and were later remobilized during post-depositional diagenesis downward and incorporated into the phosphate minerals lattice. At the same time, the presence of very depleted shale layers (below 70 ppm REE) alternating with other enriched shale horizons suggests that the process of remobilization and diagenesis was not, and could not be, a smooth and continuous one, but a rather ‘pulsating’ activity depending on the favourability of the prevailing physico-chemical conditions. These shales are presumably the weathering products of a pre-existing rock of acidic nature (e.g. granite).

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Table 2
Stratigraphic succession of Abu-Tartur phosphorites

Unit	Occurrence	Age
Aeolian sands and dunes	Depression and scarp face	Recent
Karkur formation (reefal L.S.)	Plateau and top scarp	Paleocene
Dakhla formation (shale)	Slope surface of scarp	Maestrichtian
Phosphate formation		
(Shale & phosphorite	Slope surface of scarp	Maestrichtian
Nubia formation (clays)	Foot scarp	Pre-Maestrichtian
Nubia formation (S.S. & clay)	Depression	Pre-Maestrichtian

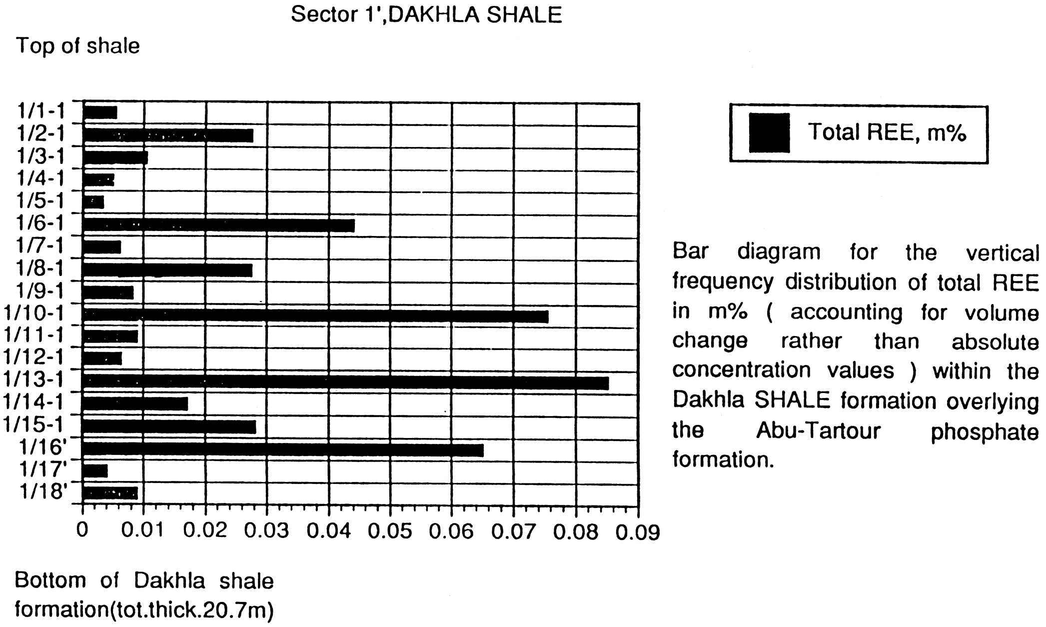

Fig. 2. Bar diagram for the vertical frequency distribution of total REE in *m*% (accounting for volume change rather than absolute concentration values) within the Dakhla shale formation overlying the Abu-Tartur phosphate formation.

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References

[1] A.A. Dardir, S.M. Kobtan, Annals Geol. Survey Egypt 10 (1980) 909.
[2] A.A. Fakhry, Abstracts, XXIV Coll. Spectroscop. Intern., Garmisch, FRG. 1985, p.45.
[3] M.A. Eid, M.M. Aly, A.A. Fakhry, K. EL-Behery, S.A. Soliman, J. Anal. Atom. Spectroscopy 3 (1988) 453–457.
[4] A.A. Fakhry, K. El-Behery, M.A.J. Eid, J. Less Common Met. 148 (1989) 59–65.
[5] S.M. McLennan, Mineralogical Soc. Am. 21 (1989) 169–200.
[6] L.A. Gromet, R.F. Dymek, L.A. Haskin, R.L. Korotev, Geochim. Cosmochim. Acta. 48 (1984) 2469–2482.
[7] L.A. Haskin, T.R. Wildeman, M.A. Haskin, J. Radioanal. Chem. 1 (1968) 337–348.
[8] J.M. McArthur, J.N. Walsh, Chem. Geol. 47 (1984) 191–220.
[9] D.Z. Piper, Chem. Geol. 14 (1974) 285–304.
[10] R.L. Cullers, S. Chaudhuri, B. Arnold, M. Lee, C.W. Wolf, Geochim. Cosmochim. Acta 39 (1975) 1691–1703.
[11] J.M. Martin, O. Hogdahl, J.C. Philppot, J. Geoph. Res. 81 (1976) 3119–3124.
[12] H.W. Nesbitt, Nature 279 (1979) 206–210.
[13] I.R. Duddy, Chem. Geol. 30 (1980) 363–381.
[14] Y. Kolodny, Phosphorites, in: C. Emiliani (Ed.), The oceanic lithosphere, Wiley Interscience Publication, 1981, pp. 981–1024.
[15] P. Henderson, Rare Earth Elements Geochemistry, Elsevier, Amsterdam, 1985, p. 510.
[16] J. Schieber, Chem. Geol. 69 (1988) 111–126.
[17] A.E. Milodowski, J.A. Zalasiewicz, Redistribution of rare earth elements during diagenesis of turbidite, hemipelagite mud–rock sequences of Llandovery age from Central Wales, in: A.C. Mortan, S.P. Todd, P.D. Haugton (Eds.), Developments in Sedimentary Provenance Studies, Geological Society special publication no 57, 1991, pp. 101–124.
[18] K.C. Condie, Geochim. Cosmochim. Acta 55 (1991) 2527–2531.
[19] A.S. Wassif, Ann Geol. Survey Egypt 7 (1977) 130.
[20] A. Montaser, D.W. Golighly, The significance of ICP relative to other laboratory plasmas in analytical spectrometry, in Radiation Chemistry: Pricinples and Applications, VCH Publishers 1987, pp. 1–15.
[21] J.A.C. Broekaert, F. Leis, L. Laqua, Spectrochim. Acta 34B (1979) 73–84.
[22] L.B. Brenner, A.E. Watson, T.W. Steele, E.A. Jones, M. Gansalves, Spectrochim. Acta. 36B (1981) 785–797.
[23] A. Bolton, J. Hwang, A.V. Voet, Spectrochim. Acta. 38B (1983) 165–174.
[24] S.J. Buchanan, L.S. Dale, Spectrochim. Acta. 41B (1986) 237–242.
[25] M.A. Eid, A.A. Fakhry, A.A. Mahdy, K.A. Eid, J.A.C.-Fresenims Broekaert, J. Anal. Chem. 351 (1995) 190.