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A FIELD TEST FOR RARE-EARTH ELEMENTS

E.R. ROSE



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A FIELD TEST FOR RARE-EARTH ELEMENTS

Abstract

A new method of detecting rare-earth elements by means of a simple chromatographic test using Arsenazo III paper is described. The test, designed by the writer to assist in his study of the geology of rare-earth deposits in Canada, may be of help to other geologists and prospectors who are also investigating the rare-earth elements. The test may be done at the outcrop in a few minutes, or later at base camp or office. Although the test is not completely specific, it is so close to being so that it is most useful in indicating the presence of rare-earth elements in rocks and minerals of unknown composition. In the absence of interfering elements, the test is sensitive to a lower limit in the range of 50 to 100 ppm, but with interfering elements in excess, as is the case with many minerals and rocks, a more practical lower limit of detection is in the range of 1000 to 5000 ppm (0.1 – 0.5 per cent) rare-earth elements. Since the test is subject to many possible interferences and difficulties, it should be used with discretion only as a preliminary, qualitative indicator of rare-earth elements.

Résumé

L'auteur décrit une nouvelle méthode pour détecter les terres rares à l'aide d'un simple essai chromatographique utilisant le papier Arsenazo III. Cet essai, conçu par l'auteur pour faciliter son étude de la géologie des gisements de terres rares au Canada, peut être utile à tous les géologues et aux prospecteurs qui recherchent ces éléments. L'essai peut être mené en quelques minutes sur le lieu de l'affleurement, ou plus tard, au camp de base ou au bureau. Bien que l'essai ne soit pas absolument spécifique, il est si près de l'être qu'il est des plus utiles pour indiquer la présence de terres rares dans des roches et des minéraux de composition inconnue. En l'absence d'éléments perturbateurs, l'essai peut déceler des teneurs de l'ordre de 50 à 100 ppm; mais, s'il y a trop d'éléments perturbateurs, comme c'est souvent le cas pour les minéraux et les roches, la limite pratique de sensibilité se situe entre 1000 et 5000 ppm (0.1 – 0.5%), pour la teneur des éléments des terres rares. Les résultats de l'essai peuvent être affectés par un certain nombre de perturbations et de difficultés, il est donc prudent de l'utiliser seulement comme un indicateur préliminaire et qualitatif de la présence de terres rares.

INTRODUCTION

The 16 rare-earth elements, lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm)¹, samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu), and yttrium (Y), form an important group of trace elements in rocks of the earth's crust that are seldom reported in chemical, spectrographic, or X-ray fluorescence analyses unless special techniques are used for their determination. Of these, cerium, lanthanum, neodymium and yttrium are by far the most common. They are not readily recognizable in many of the rocks and minerals in which they occur, and it is quite possible that occurrences of rare-earths may not be discovered in regional surveys and prospecting. Several large rare-earth deposits are now known that were

overlooked in the past because they were not recognized as such. These include the great bastnaesite orebody at Mountain Pass, California, and the monazite ore of the Kangankunde Hill carbonatite in Malawi, Africa, both of which contain from 1 to 10 per cent or more rare-earth elements. Thus, an inexpensive field test for the detection of rare-earth elements may be extremely important to the geologist and prospector, both for detecting and outlining rare-earth deposits and in screening large numbers of samples for more precise and expensive laboratory analyses.

The results of previous chemical tests to detect the elements cerium and yttrium were not completely satisfactory (Rose, 1969). A continuation of the effort, however, resulted in the development of the chromatographic method described in this paper. The work was done intermittently with the part time assistance of Messrs. F. Chan, during the winter of 1972, and D. Player, during the summer of 1974. The writer has benefited from discussions and support of colleagues in the chemistry and geochemistry sections of the Geological Survey of Canada throughout this work.

In its simplest form the test is made by grinding the sample of mineral or rock to a very fine powder, dissolving a small portion of the powdered sample in

¹A sample of promethium was not available for testing. It is best known as radioisotope products, of short half-life, of nuclear fission of uranium, but it has also been reported in very faint traces in natural occurrences of rare-earth and uranium ores.

Table 1

Colours given by Nitric Acid solutions of rare-earth and other elements on
Arsenazo I and Arsenazo III paper

Element		1% Weight/Volume Solution in HNO ₃	Colour on Arsenazo I Paper (0.25%)	Colour on Arsenazo III Paper		
				(0.5%)	(0.25%)	(0.1%)
Rare-Earth Elements	Cerium Group	Lanthanum	Violet	Dark Green	Green	Pale Green
		Cerium	Violet	Dark Green	Green	Pale Green
		Praseodymium	Violet	Dark Green	Green	Pale Green
		Neodymium	Violet	Dark Green	Green	Pale Green
		Promethium	-----	-----	-----	-----
	Yttrium Group	Samarium	Violet	Dark Green	Green	Pale Green
		Europium	Violet	Dark Green	Green	Pale Green
		Gadolinium	Violet	Dark Green	Green	Pale Green
		Terbium	Violet	Dark Green	Green	Pale Green
		Dysprosium	Violet	Dark Green	Green	Pale Green
		Holmium	Violet	Dark Green	Green	Pale Green
		Erbium	Violet	Dark Green	Green	Pale Green
		Thulium	Violet	Dark Green	Green	Pale Green
		Ytterbium	Violet	Dark Green	Green	Pale Green
		Lutetium	Violet	Dark Green	Green	Pale Green
Yttrium	Violet	Dark Green	Green	Pale Green		
Related rare Elements	Scandium	Violet	Pale Green	Pale Green	Pale Green (Dark Rim)	
	Thorium	Blue-Violet	Dark Green	Green	Pale Green	
	Uranium	Dark Green	Dark Green	Yellow-Green	Pale Yellow-Green	
Major Rock-forming Elements	Silicon	Pink	Violet	Pink	Pale Pink	
	Aluminum	Violet	Blue-Violet	Blue	Pale Blue	
	Calcium	Mauve	Grey-Blue	Grey-Blue	Pale Grey-Blue	
	Magnesium	Mauve	Violet	Violet	Pale Violet	
	Sodium	Pink	Violet	Pink	Pale Pink	
	Potassium	Pink	Violet	Pink	Pale Pink	
	Iron	Dark Blue	Grey-Blue	Grey-Blue	Pale Grey-Green	
Minor Trace Elements	Titanium	Pink	Violet	Pink	Pale Pink	
	Vanadium	Pink	Violet	Pink	Pale Pink	
	Chromium	Grey-Blue	Violet	Pink	Pale Mauve	
	Nickel	Mauve	Violet	Violet	Pale Violet	
	Cobalt	Mauve	Violet	Violet	Pale Violet	
	Manganese	Mauve	Grey	Violet	Pale Grey	
	Copper	Violet	Blue	Blue	Pale Blue	
	Lead	Pink	Grey-Blue	Blue	Pale Grey-Blue	
	Zinc	Pink	Violet	Violet	Pale Violet	
	Molybdenum	Pink	Violet	Pink	Pale Pink	
	Tin	Mauve	Mauve	Pink	Pale Pink	
	Tantalum	Pink	Mauve	Pink	Pale Pink	
	Tungsten	Pink	Violet	Pink	Pale Mauve	
	Phosphorus	Pink	Violet	Pink	Pale Pink	
	Mercury	Violet	Violet	Violet	Pale Mauve	
Cesium	Pink	Mauve	Pink	Pale Pink		
Barium	Pink	Violet	Violet	Pale Violet		
Boron	Pink	Violet	Pink	Pale Pink		
Rubidium	Pink	Mauve	Pink	Pale Pink		
Silver	Mauve	Buff (Red Rim)	Buff (Red Rim)	Straw (Pink Rim)		
Niobium	Pink	Mauve	Pink	Pale Pink		
Hafnium	Pink	Mauve (Violet Rim)	Pink (Violet Rim)	Pale Pink (Violet Rim)		
Zirconium	Violet	Dark Green	Green	Pale Green		

concentrated hydrochloric acid, and transferring a drop of the resulting acid solution to a previously prepared piece of Arsenazo III paper. The qualified presence of rare-earth elements in solution is indicated by the immediate appearance of a green spot on the violet paper, as the drop begins to dry. The test must be qualified to the extent that uranium, thorium, zirconium and to a lesser degree scandium also gave green colours similar to those of the rare-earths. Certain other elements such as iron, copper, aluminum and calcium, and combinations of them, may produce troublesome interfering colours also, when they are greatly in excess of the rare-earth elements present, especially if the rare-earth concentration is less than 0.5 per cent. At higher rare-earth concentrations the masking effect is less evident, and the test is normally quite effective.

HISTORY OF DEVELOPMENT

Previous Work

The possibility of using azoic dyes on rare-earth analysis was first brought to the writer's attention through an article by Jean Loriers (1964, p. 357) who considered the use of the organic acid Arsenazo (Neothorin) by Kuznetsov (1941, 1952) in rare-earth analyses. Abbey (1964) used Arsenazo III in the photometric determination of thorium in rocks, and drew attention to Savvin's work (1959, 1961) which presented information on producing Arsenazo III. Savvin's definitive works on Arsenazo III and derivatives were published in Moscow in 1966 and 1971. Chromatographic techniques for base-metal prospecting were described by Ritchie (1964), and attempts to use chromatography on thin layer liquid ion exchangers in mineral analysis were reported by Devries and Sijperda (1966). These reports gave substance for continued experimentation.

Present Experimental Work

First attempts to use the Arsenazo compounds in acid, neutral and basic solutions (Rose, 1969) gave variable colours in test tube and spot plate tests, that were not sufficiently distinctive to be useful in identifying cerium, lanthanum and yttrium. The available Arsenazo III being used proved to be impure, and the method was not investigated further until the winter of 1971-72, when new supplies of Arsenazo I and III were obtained which gave more consistent results. The rare-earth elements in a strong acid solution (pH 1-3) of Arsenazo I gave an orange to pink solution which, when made basic, changed to a violet coloured solution and precipitate. However, in an acid solution of Arsenazo III the rare-earths produced a blue¹ coloured solution which, when made basic, changed to a grey-blue solution and precipitate. When other elements were tested in acid solution it was found that a red or

pink colour was common to many of them with Arsenazo I, but with Arsenazo III only thorium shared the same blue colour as the rare-earths, uranium being green. This test appeared to be distinctive and promising. To make it simpler and more effective as a field test, an attempt was then made to make it chromatographic on paper stained with Arsenazo. Filter papers of several grades immersed in aqueous solutions of Arsenazo I and III, when removed and allowed to dry, were stained pink and violet respectively, their colours deepening with the concentration of Arsenazo used. Although other papers were used, Whatman no. 541 filter paper was found to take the stains most uniformly. When acid solutions of cerium or yttrium were brought into contact with these dry Arsenazo papers the colours changed to violet on Arsenazo I and green on Arsenazo III in each case, the colours diminishing as the solutions were diluted.

One per cent solutions of each of the rare-earth elements, except promethium, were prepared by dissolving, or partly dissolving, their oxides in hot concentrated nitric acid, fortified with a few drops of hydrogen peroxide where necessary to ensure solution. Each of the resulting 15 rare-earth solutions tested violet on Arsenazo I and green on Arsenazo III papers. The process was repeated using each of the available chemical elements in the laboratory. Eventually, 33 other elements were tested, including all of the major and many of the minor elements of the earth's crust. Of these a number of elements, such as aluminum, zirconium, copper and iron, gave violet or deep colours that could either be confused with, or mask, those of the rare-earths on Arsenazo I. Only uranium, thorium, zirconium and scandium, however, gave green colours similar to those of the rare-earths on Arsenazo III paper. On Arsenazo I paper, uranium tended to deviate from the rare-earths giving a greenish spot, and thorium a deep blue. These results are summarized in Table 1, and shown on Plate 1.

Tests in which the concentration of Arsenazo III was varied were also made. At a 1 per cent concentration² the colours of both the Arsenazo III and the spots are very dark and difficult to distinguish; at 0.1 per cent Arsenazo III paper is a pastel shade of violet, very sensitive to colour change, but the yellowish grey-green of iron is more noticeable. The most effective concentration appeared to be about 0.25 per cent Arsenazo III, but a range of concentrations from 0.1 to 0.5 per cent may be used.

A few tests made by varying pH values from 1 to 7 showed little change in colour, however, best results were obtained when pH values ranged from 1 to 5. As the concentration of the metal in solution is decreased the pH of the solution becomes more important in controlling the reaction and the resulting colour of the spot, but when metal concentrations are greater than 0.5 per cent the pH effect is compensated. Later, several different brands of Arsenazo III were tested, and the

¹Praseodymium and neodymium gave slightly greenish blue solutions.

²Per cent is the number of grams of material dissolved per 100 ml water.

Table 2

Colours given by some rare-earth minerals and rocks on Arsenazo I and Arsenazo III paper

Rock or Mineral and Locality	Rare Element Content	Colour on Arsenazo I Paper		Colour on Arsenazo III Paper	
		HNO ₃ Soln	HCl Soln	HNO ₃ Soln	HCl Soln
¹ Monazite Sand Brazil	>10% REE ¹ CE Group High, Th, Ti, Zr, P	Mauve	Pale Pink	Green + ²	Green +
² Monazite Sand Australia	>10% REE CE Group High, Th, Ti, Zr, P	Mauve	Pale Pink	Green +	Green +
³ Bastnaesite California	>10% REE CE Group High, Ca, Ba, Sr, P	Mauve	Pale Pink	Green +	Green +
⁴ Fergusonite Quebec	>10% REE Y Group High Nb, Th, U, Ti	Violet-Blue	Violet	Green +	Green +
⁵ Euxenite Ontario	>10% REE Y Group High, >10% Ti, Nb, U, Th	Mauve	Mauve	Grey -	Grey-Green + (hot)
⁶ Samarskite Quebec	>10% REE Y and CE Group >10% Nb, U, Th, Fe	Mauve	Mauve	Buff -	Green +
⁷ Lyndochite Ontario	>10% REE Y and CE Group >10% Th, U, Nb, Ti	Mauve	Violet	Pale Green +	Green +
⁸ Pyrochlore Nb-Ore Quebec	>2% REE CE and Y Group Nb, Ti, Ca, Na	Violet	Violet	Pale Green ?	Green +
⁹ Pitchblende U-Ore Saskatchewan	<0.1% REE >0.1% U, Th, Ca, Fe	Dark Green	Dark Violet	Pale Green +	Green +
¹⁰ Uraninite, Etc. U-Ore Ontario	<0.1% REE >0.1% U, Th >10% Si, Fe	Violet	Mauve	Pale Green +	Green +
¹¹ Uranothorite U-Ore Ontario	<0.5% REE >0.5% U, Th >10% Si, Al	Violet-Blue	Mauve	Green +	Green +
¹² Ellsworthite Ontario	>0.1% REE CE and Y Group >10% Nb, U, Ta, Fe, Ti	Violet-Blue	Mauve	Grey-Blue -	Grey-Green + (hot)
¹³ Allanite Quebec	>2% REE CE and Y Group >10% Si, Al, Fe, Ca	Dark Violet	Mauve	Green +	Green +
¹⁴ Allanite in Pegmatite Quebec	<1% REE >10% Si, Al, Fe, Ca	Dark	Mauve	Yellow-Green ?	Green +

Table 2 (cont'd.)

Rock or Mineral and Locality	Rare Element Content	Colour on Arsenazo I Paper		Colour on Arsenazo III Paper	
		HNO ₃ Soln	HCl Soln	HNO ₃ Soln	HCl Soln
¹⁵ Chevkinite Quebec	>6% REE CE and Y Group >10% Si, Al, Fe, Ca	Violet-Blue	Violet	Green +	Green +
¹⁶ Eudialyte Quebec	>2% REE CE and Y Group >10% Si, Be, Zr	Violet-Blue	Violet	Green +	Green +
¹⁷ Sphene Ontario	>1% REE CE and Y Group >10% Ca, Ti, Fe, Si	Violet-Blue	Dark Violet	Pale Violet -	Green +
¹⁸ Black Garnet Quebec	<1% REE Y Group, Fe, Al, Si	Dark	Dark	Yellowish Green ?	Yellowish Green + (hot)
¹⁹ Brown Apatite Ontario	<1% REE CE Group, Ca, P	Pink	Pink	Blue-Green ?	Blue-Green + ?
²⁰ Black Phosphate Rock Idaho	<0.01% REE Ca, Al, Si, P	Pink	Pink	Grey-Blue ?	Grey-Blue ?
²¹ Titaniferous Magnetite Quebec	REE ? >30% Fe, Ti, Cr, V	Dark	Violet	Grey (Violet Rim) -	Grey-Green Yellow-Green (hot)?
²² Titaniferous Magnetite Quebec	REE ? >50% Fe, Ti, Cr, V	Dark	Violet	Grey (Violet Rim) -	Grey-Green Yellow-Green (hot)?

¹REE = Rare-earth elements.

²+, -, ? signs indicate whether test for rare-earths was positive, negative, or indeterminate, respectively.

colours were found to vary slightly with the brands, as well as with the concentration of reagents and metals.

A number of the tests were made using papers prepared from mixtures of Arsenazo I and III solutions with concentrations of 0.3 per cent. In the proportion of Arsenazo I: Arsenazo III of 1:4, the paper was violet coloured and the rare-earth spots were bluish instead of green; in proportions of 1:3, 1:2, and 1:1, both papers and rare-earth spots were progressively paler pink, and violet, respectively. Because elements such as aluminum, calcium, copper, lead, zinc and molybdenum produced similar bluish or violet spots with these Arsenazo I and III mixtures, this method was not considered to be diagnostic for rare-earths and was discontinued.

Next, mixtures of rare-earth elements and mixtures of rare-earths with other elements were tested. Rare-earth mixtures reported green with Arsenazo III paper, as did those of uranium and thorium, except when the

rare-earths were at low concentrations and interfering elements were greatly in excess. At concentrations of less than 0.1 per cent rare-earth elements, and more than 5 per cent interfering elements, the rare-earth green was difficult to detect, but at higher rare-earth element concentration this interference was less evident.

The lower limit of detection for a neodymium solution on Arsenazo III paper was found to be about 0.005 per cent neodymium at pH 5, and about the same for thorium. A more practical lower limit of detection, however, is about 0.01 per cent rare-earth elements in solutions that are free of interfering elements, and about 0.1 per cent for solutions with more than 1 per cent interfering elements.

After a period of inactivity the testing program was resumed in 1974 when three different brands of Arsenazo III were obtained. The formation of a green colour on Arsenazo III paper from the three brands was characteristic of each of the rare-earths, and the

Table 3

Arsenazo III tests on assorted rocks and ore minerals

ROCK OR ORE MINERAL	LOCALITY	ARSENAZO III TEST IN HCl SOLUTION		ANALYSIS ¹ FOR RARE ELEMENTS %
1. Gossan on shale	Barn Mt., Yukon	Mauve to bluish	- ² REE ³	-; U, Zr trace
2. Ti-magnetite in gabbro	Banks Is., B. C.	Yellowish green ⁴	- ² REE	-; Sc 0.004
3. Cu-V argillite	Quadra Is., B. C.	Bluish	- REE	-; Zr trace
4. Ti-magnetite in gabbro	East Sooke, B. C.	Yellowish green ⁴	- ² REE	0.06
5. Sn-rhodonite vein in granite	Tsitsutl Mt., B. C.	Mauve	- REE	-
6. Purple fluorite and pyrite	Birch Island, B. C.	Pale bluish green	+ REE	0.75; U trace, Th 0.04
7. Ochre on shale	Rocky Mt. Trench, B. C.	Buff	- REE	-
8. Phosphatic nodule in shale	Crowe Mine, Alberta	Bluish green	+ REE	0.15; Zr 0.02, Sc 0.008
9. Dolomite nodule in shale	Crowsnest Lake, Alberta	Greyish blue	- ² REE	-; but Y trace; Zr 0.04
10. Rusty grey siderite	Wawa, Ontario	Yellowish green ⁴	- ² REE	-
11. Rusty pink carbonate vein	Firesand Creek, Ontario	Bluish green	+ REE	0.21; Th 0.03, Zr 0.04
12. Granular apatite-magnetite	Nemegos, Ontario	Yellowish green ⁴	- ² REE	0.16; Th 0.01, Zr 0.02
13. Massive magnetite	Nemegos, Ontario	Yellowish green ⁴	- ² REE	-; Zr trace
14. Radioactive carbonate-chlorite vein	Montreal Harbour, Ontario	Bluish green	+ REE	0.035
15. Radioactive skarn	Bancroft, Ontario	Bluish green	+ REE	0.03; Zr trace, Sc 0.005
16. Granite, with sphene	Carp, Ontario	Mauve to pale green	+ REE	0.045; Zr 0.04
17. Radioactive grey dolomite	March tp., Ontario	Grey to bluish green	+ REE	0.025; U 0.06
18. Radioactive granite-pyroxenite	Grand Remous, Québec	Pale grey-green	+ REE	0.075; U 0.01, Th 0.1
19. Ilmenite in anorthosite	Ivry, Québec	Yellowish green ⁴	- ² REE	-; Sc 0.005
20. Ti-magnetite in gab. anorthosite	Magpie Mt., Québec	Yellowish green ⁴	- ² REE	-; Zr 0.02, Sc 0.003
21. Manganiferous shale	Manuels Brook, Nfld.	Buff	- REE	-; Sc 0.004
22. Grey barite and carbonate	Barite Mt., Yukon	Mauve	- REE	-
23. Radioactive pitchblende ore	Uranium City, Sask.	Green	+ REE	0.035; U 2.0, Zr 0.02
24. Radioactive conglomerate ore	Elliot Lake, Ontario	Green	+ REE	0.44; U 0.2, Th 0.1, Zr 0.01
25. Spotted grey-white carbonate	Bond zone, Oka, Québec	Green	+ REE	0.65; Nb 1.0, Zr 0.04
26. Nepheline syenite (ijolite)	Main zone, Oka, Québec	Pale Mauve	- REE	-; Sc -; Zr 0.01.
27. Nepheline syenite pegmatite	Mont Saint Hilaire, Québec	Pale grey-green	+ REE	0.685; U trace; Th trace
28. Carbonate zone, 50' chip sample	Huddersfield tp., Québec	Pale grey-green	+ REE	0.185; Th 0.01, Zr trace
29. Radioactive fergusonite pegmatite	Evans-Lou mine, Québec	Deep green	+ REE	2.62; U 0.3, Th 0.3
30. Allanite pegmatite, chip sample	Lac à Baude, Québec	Green	+ REE	0.06; Zr 0.05

¹X-ray fluorescence analyses, by E. J. Brooker, X-ray Assay Laboratories, Don Mills, Ontario.²+, -, ? signs indicate whether rare-earth test was positive, negative or indeterminate, respectively.³REE = Rare-earth elements.⁴High iron content masks.

elements, uranium, thorium, zirconium and scandium, when present in nitric acid and hydrochloric acid solutions. However, because the shade of green produced varied slightly with the brand and with the concentration of Arsenazo III being used, it is advisable to use a standard rare-earth solution to compare the colour produced on the Arsenazo III paper being used.

Application to Minerals and Rocks

With this favourable chemical evidence it was necessary to determine if the test would be successful with the complex chemical assemblages of rocks and minerals. The effectiveness of nitric acid as a solvent for some of these materials was also questionable. Some of the tests indicated that hydrochloric acid might be better. Accordingly, 20 samples of complex, rare-earth-bearing rocks and minerals with a rare-earth content ranging from 10 per cent to less than 0.01 per cent and a great number of interfering elements of the rare-earths were tested individually with concentrated nitric acid and with concentrated hydrochloric acid. The results are shown in Table 2 and on Plate 2.

Nitric Acid Versus Hydrochloric Acid

In nitric acid, 11 of 20 samples gave positive tests, 4 negative, and 5 indeterminate; in hydrochloric acid, 17 were positive, 2 of these, euxenite and ellsworthite, had to be heated, and 3 were indeterminate. The latter three ranged from about 1 to less than 0.01 per cent rare-earth elements and from 50 to 80 per cent interfering elements. Hydrochloric acid is thus much more effective as a solvent than is nitric acid and may be used with considerable success even without heating. The performance of both acids is generally improved with heating.

Minerals with a high iron content such as titaniferous magnetite have a greater tendency to produce a yellowish or brownish colour when hydrochloric acid is used as the solvent. The colour may interfere with the rare-earth green, but it usually does not appear until several hours after the spot has dried in contrast to the colour of the rare-earths which appears almost instantaneously, especially when the rare-earths are present in high concentrations.

Iron Formations

A group of 21 samples of iron formations from northern New Brunswick were obtained courtesy of Dr. D.F. Sangster. These samples were supplied to the Geological Survey of Canada by Dr. Brian Skinner of Yale University for further analyses of the major elements, and Mr. C.R. McLeod provided the writer with small portions of these for test purposes on the rare-earths. These samples had been analyzed for 15 elements including 7 rare-earth elements and scandium and thorium by instrumental neutron activation methods for Joseph L. Graf, Jr. in the laboratories of Yale University in 1974. They had been found to range from 0.0005 to 0.033 per cent rare-earth elements, from 0 to

0.001 per cent scandium, from 0 to 0.0018 per cent thorium, and from 9 to 50 per cent iron. When tested by the writer on Arsenazo III paper all samples were initially negative, but after several hours a green colour began to appear in 4 of the samples, after 2 days, 11 were green, and after several days all showed a shade of green. None of the green colours, however, were sufficiently distinctive to be indicative of rare-earths, and 9 were sufficiently yellowish green that iron was suspected as the cause. In all of these samples the ratio of iron to rare-earths is very high, and the rare-earth content is low, so although the rare-earths seem to be reporting faintly they are probably beyond the effective lower limit of the field test for most samples. Nevertheless the green colours produced were probably not solely due to their iron content.

Other Rocks

A group of 30 samples (Table 3) of assorted rocks and ore minerals of various types from localities across Canada were tested using Arsenazo III paper, and were submitted later to an independent laboratory for rare-earth element analyses. Fifteen of the samples were rare-earth positive on Arsenazo III paper, nine were indeterminate, and six were negative. Analytical results by X-ray fluorescence (Table 3) indicated that the 15 positive samples were rare-earth bearing, 3 of the 9 indeterminate samples were rare-earth bearing, and the 6 negative samples were rare-earth negative. The analytical results indicate that 18 of the samples carry rare-earth elements in amounts ranging from 0.01 to 2.62 per cent. Because the detection limits of the individual rare-earth elements ranged from 0.005 to 0.01 per cent in this method of analysis, it is possible that 6 or more of the indeterminate or negative samples also carried traces of rare-earths.

DETAILED METHOD OF TEST

Materials Required

Table 4 presents the essential and optional reagents and equipment required to detect rare-earths using this chromatographic technique.

Preparation of Test Solutions and Papers

A 0.25 per cent solution of Arsenazo III is prepared by dissolving 0.25 g of the compound in 100 ml of distilled water. A filter paper (Whatman no. 541, 12.5 cm diameter) is immersed in the solution until the paper is uniformly soaked, and then it is removed with tweezers and hung to dry. The resulting Arsenazo III paper is violet in colour.

Arsenazo I paper may be prepared in a similar manner, dissolving 0.25 g of Arsenazo I in 100 ml of distilled water. The resulting Arsenazo I paper is pink in colour.

The test papers may be made up in batches and stored in the filter paper boxes until required, at which time they may be spot tested by transferring drops of

Table 4
Reagents and equipment required for rare-earth tests

Reagents	
<u>Essential</u>	<u>Optional</u>
Concentrated hydrochloric acid (HCl) Distilled water (H ₂ O)	Concentrated nitric acid (HNO ₃) Hydrogen peroxide (30% H ₂ O ₂) Sodium carbonate (Na ₂ CO ₃)
Arsenazo III - 2, 2' (1, 8 ³ -dihydroxy-3, 6-disulfonaphthalene-2, 7 diazo) - dibenzearsonic acid $C_{22}H_{18}O_{14}N_4S_2As_2$	Arsenazo I - (o{(1, 8-dihydroxy-3, 6-disulfo-2 naphthyl) azo } benzearsonic acid, trisodium salt) $C_{16}H_{10}O_{11}N S_2As Na_3$
Equipment	
<u>Essential</u>	<u>Optional</u>
Small mortar and pestle or small steel plate 2 pyrex beakers, 30 ml size 2 glass or plastic dropping bottles 1 package filter paper, Whatman no. 541 1 pair tweezers or forceps 1 stirring rod 2 saucers or watch glasses	Small porcelain crucible 1 funnel, glass or plastic, medium size 1 medicine dropper 1 measuring scoop, spatula

test solutions to the paper, or cut into thin strips that may be dipped into the solution to be tested. Any excess Arsenazo solutions may be stored in closed bottles for future use.

Preparation and Treatment of Sample

(1) A representative portion of the sample is crushed and powdered as finely as possible in a small mortar, or on a small steel plate. A small portion of this sample (25 to 50 mg) is placed in a small pyrex beaker or test tube into which about 5 to 10 ml of concentrated hydrochloric acid or nitric acid are stirred slowly. Caution must be taken at this point to avoid explosive reactions. After a few minutes a drop of the solution is transferred to previously prepared dry Arsenazo paper, and the colour is noted. It should be noted that materials of low rare-earth concentration may require longer immersions in acid for best results.

(2) If the sample does not dissolve in either nitric or hydrochloric acid the mixture is heated strongly for several minutes using a small gas torch or other heat source. Two or three drops of concentrated hydrogen peroxide may be added to aid in dissolution of the sample. In most cases the sample will now be partly dissolved, and the solution probably will be coloured. If so it may be either filtered or allowed to settle in order to decrease any turbidity or strong

colour present. A drop of the clarified solution is transferred by means of a glass rod onto the dry Arsenazo paper, and the resulting colour is noted. The colour may change slowly so it is best to note the colour again later. A green colour appearing quickly is indicative of rare-earth elements; uranium, thorium, scandium and zirconium may be present, but zirconium is unlikely to be in solution at this stage.

(3) If the test is still indeterminate, the sample may be dried (or a new sample taken), mixed with one half its volume of flux, such as sodium carbonate, sodium pyrophosphate, or sodium peroxide, and then heated to fusion. The resulting fused product is cooled, crushed and ground to a fine powder that is treated dropwise as in step 2 with 1:1 nitric acid. The resulting solution is spotted on Arsenazo paper, and the colour noted.

(4) The individual spots may be numbered corresponding to the samples, acids and fluxes used, and the specifications of the Arsenazo paper as well as the date and number of the test may be printed on the test paper to provide a useful record for reference. A record of the method of testing each sample should be kept.

(5) In addition, for best results, the effect of standard solutions on the test may be compared directly with that of the unknown sample.

(6) If the test is positive, and if another test such as described by Rose (1969) suggests the presence of cerium or yttrium, the presence of rare-earth elements is strongly indicated.

DESCRIPTION OF THE TEST

Arsenazo III Test

When a tiny drop of the acid solution of the material, rock or mineral, to be tested is transferred by means of a thin glass rod to the surface of the Arsenazo III test paper, it forms a circular spot of various colours depending on the elements present in solution. It is best to compare the results of prepared solutions of known rare-earth elements on the particular test paper being used because the colours are dependent on the brand of Arsenazo III and the strength of the reagents being used. At the Arsenazo concentrations suggested (0.25 per cent), concentrated nitric acid or hydrochloric acid form reddish spots on Arsenazo III paper; concentrated ammonium hydroxide or sodium hydroxide, grey-blue spots; if rare-earth elements, uranium, thorium, or zirconium are present in solution, a bright green spot will quickly form; and a pale green spot of scandium is present. None of the 33 other elements tested by the writer in nitric acid solution had a similar effect, except perhaps for iron which under certain conditions gave a faintly grey-blue or grey-green spot, the colour appearing very slowly, a day or more after the spot had dried. This effect was more notable when dilute solutions of Arsenazo III were used which may be troublesome if small unknown quantities of rare-earths are present with iron in the solution. A yellowish green spot is suggestive of iron. A number of other elements such as aluminum, calcium, magnesium, nickel, cobalt, manganese, copper, lead, zinc and barium, gave bluish or violet coloured spots, which may in some cases interfere with, or be confused with, the green colour of the rare-earth element spots. The most troublesome were the blue colours of copper, aluminum, and calcium.

Arsenazo I Test (optional)

Because of interferences from iron and other elements, Arsenazo I test paper is not very helpful, but it may be used to attempt to distinguish between uranium and thorium and some other elements. Nitric acid or hydrochloric acid have little effect on the pink coloured Arsenazo I paper, but acid solutions of the rare-earth elements as well as thorium, zirconium and scandium produce violet spots (thorium usually being slightly deeper and bluer). Uranium produced a dark green stain, iron a dark grey-blue, chromium a grey-blue, and a number of other elements such as aluminum, calcium, magnesium, copper, and mercury gave deep blue-violet colours capable of masking the rare-earths and each other. The Arsenazo I tests are more effective in nitric acid than in hydrochloric acid.

CONCLUSION

The Arsenazo III paper test is a relatively simple and inexpensive method of detecting the presence of rare-earth elements in samples of unknown rare-earth content. However, it does not differentiate between the rare-earths, and uranium, thorium, zirconium, or scandium, but as these are all closely related to rare-earth elements, this is not too detrimental. The presence of uranium and thorium is indicated by their radioactivity; zirconium is unlikely to be present as it resists solution in hydrochloric acid and the rare scandium is considered by some to be a rare-earth element. The test is also subject to interferences from combinations of iron and other elements when the rare-earth element content is low, and difficulty may be encountered in dissolving some refractory rare-earth-bearing materials. It should be used with discretion as a preliminary, qualitative test for rare-earth elements. Some practice with known materials is required, and it is also recommended that comparisons should be made with the colours of known elements on individual Arsenazo papers.

The test may be done in the field, in simplified form, by carrying a small kit to the outcrop, or by testing samples at a base camp. The light field kit need contain only a supply of Arsenazo III paper, a small plastic bottle of concentrated hydrochloric acid, a small mortar and pestle, and a small pyrex beaker or test tube in which to dissolve the pulverized sample, in addition to a geological hammer and knife. Many of the powdered rare-earth ores and minerals will dissolve sufficiently in concentrated hydrochloric acid when ground to a very fine powder to give a positive test on Arsenazo III paper; nitric acid is not quite as effective. Fine grinding is essential to ensure effective leaching by the acid; however, heating also helps to promote leaching and solution of the rare-earth and other elements. Fusion may be necessary in a few difficult cases to obtain a positive test on a very refractory, rare-earth-bearing mineral, mineral assemblage, or rock.

NOTE

Additional sets of colour Plates 1 and 2 are available at a price of \$3.00 from the Geological Survey of Canada Publication Distribution Offices in Ottawa, Calgary and Vancouver.

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