My name is Michael Murphy and I work in the isotope laboratory in the Department of Geology, University College Dublin. I am going to talk to you about rubidium, strontium, samarium and neodymium elemental separation but before doing so I would like to deal briefly with the background to elemental separation and why it is necessary for us.

In the laboratory we have a Micromass 30 Thermal Ionisation Mass Spectrometer (TIMS). We are interested in determining the isotopic composition of Sr, Rb, Nd and Sm from various geological samples on the TIMS. However, before we can do this it is necessary to make the sample as elementally pure as possible. This is important as an impure sample will result in a very poor ion yield and beam stability in the mass spectrometer and hence a poor analysis. Isobaric interference must also be minimized for Sr & Nd isotopic analysis. This is where an isotope is common to two elements such as Rb87 & Sr87, as the mass spectrometer cannot discriminate between isotopes of the same atomic mass it is necessary to remove them chemically prior to analysis.

In the laboratory, as in most geochemical isotope laboratories, we have traditionally performed this separation procedure using ion exchange columns. Ion exchange techniques were developed in the 1950's & 60's and details published by a number of workers including F.W.E. Strelow who published this paper in 1960. In it he published this table of equilibrium distribution coefficients (Kd) for 43 cations in various concentrations of hydrochloric acid. I have highlighted the coefficients for rubidium, strontium and the rare earth elements lanthanum and cerium. The larger the coefficient, the greater the affinity the resin has for the cation. Also the larger the ratio of the coefficients of two cations, the easier it is to separate them using an ion exchange column. You can see from this table that the weaker the acid is, the greater the equilibrium distribution coefficient (Kd) is. Hence for any particular element, a weak acid solution results in much more acid being required to elute the cation from an ion exchange column than a strong acid solution of the same cation.

For our traditional ion exchange separations we used Bio-Rad AG50W-X-12 resin and a 2.5 M HCl sample solution. We found we needed 5 grams of resin in order to give us an adequate cation separation for a sample weight of 100 milligrams maximum. This resulted in 94 mls of 2.5 M HCl being required to pass through the column in order to elute Sr, with the Sr fraction being collected in the final 27 mls of 2.5M HCl. In order to elute Sm & Nd, a further 55 mls of 4M HNO3 was required with Sm & Nd being collected in the final 35 mls. The Sr fraction was put through the ion exchange resin again in order to improve the separation. The Sm & Nd fraction was then evaporated down, converted to chloride and put through an ion specific resin with the same active ingredient as

Ln resin but on a different support, in order to separate Sm from Nd. A larger column and hence more acid was required than the Ln column we presently use and which I will describe shortly.

When we in Dublin first learned of Eichrom specific ion resins and read this paper (overhead of the first page of the paper) by Christian Pin and his colleagues we were very interested in the resins and in trying to get the technique to work. This paper was followed a few years later by this paper (overhead) also by Christian Pin on ion specific resins. The first paper describes the use of Eichrom Sr resin to separate Sr from silicate samples and TRU resin to separate the light rare earth elements as a group. The second paper describes the use of Ln resin to separate the light rare earth elements (LREE) individually, in particular Nd from Sm. These resins as they have a very large equilibrium distribution coefficient for one or a small group of cations offered the possibility of;

(1) giving better separation of the required element from the dissolved rock solution and hence a more accurate and reproducible analysis on the TIMS
(2) a lot less acid required to perform the separation,
(3) lower blank as less acid was required & the resin would be discarded after each separation
(4) a faster separation procedure

The problems as we saw them were;

(1) greater expense as the resin and column was discarded after each separation,
(2) as the columns had to be made up each time it would possibly take longer to make a separation,
(3) Sr resin is not entirely specific to Sr but also retains Ba and Pb in dilute HNO3.

Overall we have managed to realize the advantages as we saw them and are very happy with the results we have obtained. This is especially true for Nd isotopic analysis where the success rate is much higher than previously obtained suggesting that a purer Nd fraction is obtained with the specific ion resins.

When we decided to try and use the Eichrom resins we had to decide at first what columns to use and how much resin. We made up a chemical solution with all the major elements in the approximate concentrations you would expect to find in a geochemical sample. We then calibrated the columns with this solution and using an inductively coupled plasma (ICP) spectrometer to detect the elements of interest and adjusted the columns and acid as was neccessary.

I would now like to describe exactly how we perform the elemental separations using Sr, TRU & Ln resins.

In order to keep costs down we decided to use a 5 ml pipette tip as a column instead of purchasing ready made columns. We cut off the top of the pipette tip, and push a porous polyethylene frit, 2.5 mm diameter down to the bottom of the tip as shown on the slide. The frit material was bought in a sheet from Bel-Art, USA, has a nominal pore size of 70 um and is 3.2 mm thick. This frit is used to keep the resin in place. Next we add in 100 mg of resin, wet it with 0.05 M HHO3, remove any air bubbles by agitating it with a glass rod and when the dilute nitric acid has flowed through the resin, we push a polyethylene frit, 6.5 mm diameter onto the top of the resin. This frit stops the resin from being disturbed when sample or acid is added to the column and is very important to ensure a smooth flow rate and good separation. The Sr and TRU columns are made in this manner. However for TRU resin as we use a finer grade resin (50-100 um instead of 100-150 for Sr) we found we had to use a 4 mm frit at the bottom of the column in order to give an adequate flow rate. This gives a column length of 20 mm for Sr & 14 mm for TRU resin. (I will then show a slide of both columns in the column holder and point out the "support" on the TRU resin column holder.) The columns are washed with 3-4 mls 0.05M HNO3 to remove any cations present, preconditioned with 1M HNO3 and are then ready for use.

The Ln resin can be reused, as indicated by Christian Pin. Hence we decided to use Bio-Rad columns as they come fitted with a frit and have room for 600 mg of resin and 10 mls of a reservoir of acid. We load the resin as a slurry, remove any air bubbles, & fit a 9 mm porous frit to the top of the resin. (Slide of full column & column holder).

The samples following standard HF+HNO3 acid digestion, are evaporated to dryness, dissolved in 6M HCL and finally in 2 mls of 1M HNO3. For the first stage in the separation procedure, the Sr columns are put on top of the TRU columns as shown above. The dissolved sample is put directly on the Sr resin top frit and the solution flows through the resin where Sr is retained, out at the bottom of the column, through the TRU resin where the LREE are retained and the remaining elements including rubidium, flow out at the bottom where they are collected if Rb is required. 1 ml of 1M HNO3 is added to the Sr resin to wash it and the solution again collected. The columns are then disassembled so that the Sr & LREE can be eluted separately. The Rb has to be separated from the collected fraction using the standard cation exchange resin as described earlier. Perhaps Eichrom will develop a Rb specific resin just for this purpose!!

Sr Elution

1. Wash the Sr.Spec columns with 3 mils of 8M HNO_3 and discard eluant.
2. Add 2 mils of 0.05M HNO_3 and collect. This fraction has to be further purified to remove Ba which can seriously affect the analysis of Sr on the mass spectrometer by reducing the yield of ions. Hence the purification process is repeated as described below.
3. Evaporate down and redissolve samples in 1 mil of 1M HNO_3.
4. Wash columns with 3 mils of 0.05M HNO_3 and discard.
5. Precondition columns with 3 mils of 1M HNO_3 and discard.
6. Load the semi-purified Sr fractions on the same columns as before ensuring that exactly the same column is used for each sample to avoid cross contamination and discard eluent.
7. Add 1 mil 1M HNO_3 and discard.
8. Add 3 mils of 8M HNO_3 and discard.
9. Add 2 mils of 0.05M HNO_3 and collect Sr.
10. Dry down the Sr fractions which are then ready for analysis on the mass spectrometer.

This gives a total acid volume of 12 mls for a double stage separation as compared to 94 mls for a single stage separation using the cation exchange resin.

Elution of LREE.

1. Wash the TRU.Spec resin with 2 mls 1.0M HNO3 and discard.

2. Then wash the TRU.Spec resin with 0.25 ml 0.05M HNO3 and discard. This is to change the acid on the resin to 0.05M HNO3 so that the 1M HNO3 will not be washed onto the LN column as this would result in the REE being washed off again very quickly and lost.

5. Position the TRU.Spec columns **on top** of the LN columns so that the REE will be washed directly from one to the next.

6. Elute the REE with 1.75 mls 0.05M HNO3.

7. Dismantle the columns.

The light rare earth elements are hence separated using 4 mls of dilute nitric acid compared to 55 mls of 4 M HNO3 for the traditional ion exchange resin column.

Elution of Nd & Sm from Eichrom LN resin column.

1. Wash with 4 X 1 ml 0.2M HCl and discard.
2. Wash with 10 mls 0.2M HCl and discard.
3. Position Nd beakers under columns. Elute Nd with 2.5 mls *0.3M HCl*.
4. Wash columns with 3 mls *0.5M HCl* and discard.
5. Position Sm beakers under columns. Elute Sm with 2.5 mls 0.5M HCl.
6. Evaporate down the Sm & Nd fractions. They are now ready for analysis on the mass spectrometer.
7. Wash the LN columns with a bowl full of 6M HCl, followed by ~ 5 mls of 0.2M HCl. Add another ~5 mls 0.2M HCl and cap the columns top and bottom in order to prevent the columns from drying out. Where possible the columns should not be left uncapped overnight.

It takes approximately a half a working day to make a set of six Sr and Tru columns. The complete chemical separation of Sr, Sm & Nd can now be done in one working day as compared to three days previously. This is mainly due to less acid being required. The fact that the solution drips directly from one column to the next without the need to evaporate down or change the anion, is the other major time and labour saving feature.