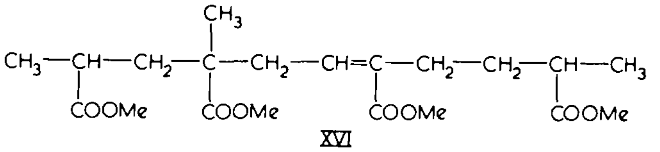
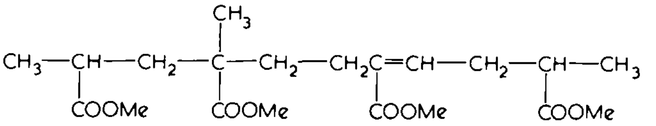
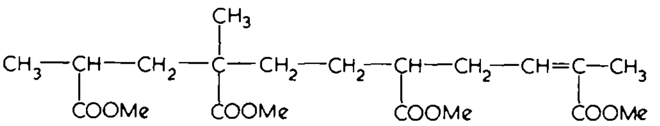

$CH_3{-}CH(COOMe){-}CH_2{-}C(CH_3)(COOMe){-}CH_2{-}CH{=}C(COOMe){-}CH_2{-}CH_2{-}CH(COOMe){-}CH_3$

XVI


$CH_3{-}CH(COOMe){-}CH_2{-}C(CH_3)(COOMe){-}CH_2{-}CH_2C(COOMe){=}CH{-}CH_2{-}CH(COOMe){-}CH_3$

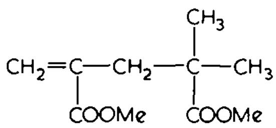
XVII


$CH_3{-}CH(COOMe){-}CH_2{-}C(CH_3)(COOMe){-}CH_2{-}CH_2{-}CH(COOMe){-}CH_2{-}CH{=}C(COOMe){-}CH_3$

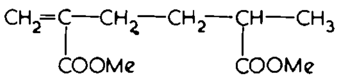
XVIII

The exact individual yields of the six isomers could not be determined, because the oxidative fragmentation reaction was not a quantitative one.

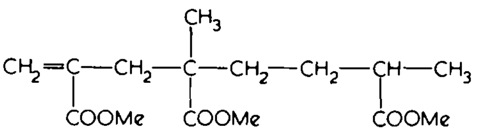
The thermal oligomerization of BaMA at 190°-240°C gave two dimers (I, II) and two trimers (III, IV). However, CaMA gave one dimer (II) and one trimer (IV) as follows[5,6]:


$CH_2{=}C(COOMe){-}CH_2{-}C(CH_3)(COOMe){-}CH_3$

I


$CH_2{=}C(COOMe){-}CH_2{-}CH_2{-}CH(COOMe){-}CH_3$

II


$CH_2{=}C(COOMe){-}CH_2{-}C(CH_3)(COOMe){-}CH_2{-}CH_2{-}CH(COOMe){-}CH_3$

III

If the tetramers are formed by the addition of trimer biradicals to the monomer, CaMA gives tetramers which belong to the group A, and BaMA tetramers which belong to both group A and group B. The formation of three isomers having a double bond at different positions may be explained by proton migration. In the solid state, different molecular microenvironments can exist in contrast to the liquid state in which the microenvironment may be considered to be uniform these difference in microenvironment may cause differences in proton migration to give the three isomers. Details on the mechanism of these tetramer formations will be reported in the near future.

REFERENCES

1 Albisetti, C. J., England, D. C., Hogsed, M. J. and Joyce, R. M. *J. Am. Chem. Soc.* 1956, **78**, 472
2 Lingnau, J., Stickler, M. and Meyerhoff, G. *Eur. Polym. J.* 1980, **16**, 785
3 Stickler, M. and Meyerhoff, G. *Makromol. Chem.* 1980, **181**, 131
4 Naruchi, K., Yamamoto, O., Miura, M. and Nagakubo, K. *Kagaku Kaishi* 1976, 1791
5 Naruchi, K., Miura, M. and Nagakubo, K. *ibid.* 1977, 871
6 Naruchi, K., Tanaka, S., Tamura, T. and Miura, M. *ibid.* 1978, 1686
7 Naruchi, K., Tanaka, S., Kobayashi, H. and Yamada, K. *ibid.* 1979, 1433
8 Naruchi, K. and Miura, M. *Polymer* 1981, **22**, 1716
9 Hill, J. W. and McEwen, W. L. 'Organic Syntheses', Col., Vol II, 1943, p 53

Thermal degradation of a series of phosphorylated resins of polyethylene

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The copper ore solutions, particularly those from Chuquicamata deposits (Chile), contain up to 15 ppm of Uranium which is covered by using ion-exchange Amberlite IRA-400. We have prepared specific resins for uranium from polyethylene phosphorylated. The recovery can be made by using the direct combustion of charged resin. This method is less expensive than the elution with acid and U_3O_8 is obtained directly.

Keywords Degradation; thermal; polyethylene; resins; thermogravimetric analysis; uranium

INTRODUCTION

Thermogravimetric analysis (t.g.a.) data provide information about the temperature at which major fragmentation occurs and is therefore an indication of the inherent stability of the polymer structure[1].

The resins used were prepared from polyethylene (DOW PE-515) phosphorylated with PCl_3 and O_2[2] and then crosslinked with ethylenediamine, ethyleneglycol, diethyleneglycol and triethyleneglycol respectively. These resins are specific for uranium, cheap and have greater maximum capacities than commercial Amberlite IRA-400[3]. In actual fact, the more often used resin for the recovery of uranium from copper solution is the Amberlite IRA-400[4]. When the resins are charged, the elution of uranium is made by such salts and acids such as: HCl, H_2SO_4 or Na_2CO_3,[5,6]; but another possibility for a rapid recovery of the metal is the direct combustion of the resin. For this reason it is important to know the thermal stability of the resins and the composition of the resulting residue.

RESULTS AND DISCUSSION

In this report the thermogravimetric data were obtained using a Thermobalance TGS-1, Perkin-Elmer Model

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with 5 mg samples heated under dynamic nitrogen (50 ml min^{-1}) at 10°C min^{-1} at 600°C. The data obtained are reported in *Figure 1* as residual weight *versus* temperature. It was observed in *Figure 1* that the improved thermal stability of these resins resulted, because at 300°C they have approximately 10% degradation. The exceptions to this were the phosphorylated polyethylene and the phosphorylated polyethylene polyethyleneglycol resins which lost 20% weight. At first, the polyethyleneglycol resins show a rapid degradation with a 15% weight loss between 100° to 300°C. The other polyesters, polydiethyleneglycol and polytriethyleneglycol show greater stability due to a possible higher molecular weight. Therefore, they show a residual weight between 16 to 32% at 600°C.

However, *Figure 2* shows the residual weight of the uranium charged resins. It was observed that the charged polyethyleneglycol resin showed a very similar decomposition plot to the uncharged resins. The polydiethyleneglycol has the largest residual weight, 62% at 600°C and if compared with the residual weight of the uncharged resins, we can conclude that this will have the highest amount of uranium (see *Table 1*). It was also observed that the lower uranium contents are in the phosphorylated resins because they are not crosslinked.

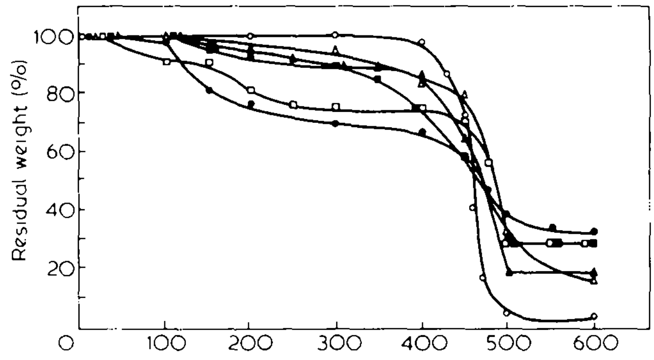

Figure 1 Thermogram of resin residual weight (%) *versus* temperature (°C). ○, Polyethylene; ●, Phosphorylated polyethylene; △, Phosphorylated polyethylene, polyethylene diamine; □, Phosphorylated polyethylene polyethylene glycol; ■, Phosphorylated polyethylene polydiethylene glycol; ▲, Phosphorylated polyethylene polytriethylene glycol

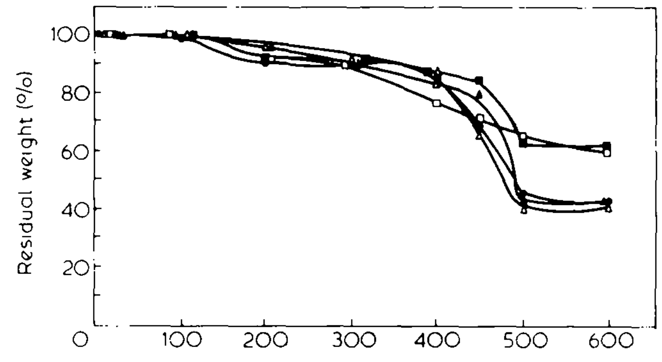

Figure 2 Thermogram of uranium charged resins residual weight (%) *versus* temperature (°C). ●, Phosphorylated polyethylene; △, Phosphorylated polyethylene polyethylene diamine; □, Phosphorylated polyethylene polyethylene glycol; ■, Phosphorylated polyethylene polydiethylene glycol; ▲, Phosphorylated polyethylene polytriethylene glycol

The uranium charged resin of phosphorylated polyethylene, polyethylenediamine was burned from 25° to 800°C in a Muffle furnace, under manual control for one hour. The residual product was analyzed by Raman spectroscopy (Raman SPEX Spectrometer COMPACT-1301, Model) and it was verified that the same residual product was formed as with the other charged resin. The Raman spectrum of this product, (*Figure 3*) shows a stretching uranium–oxygen mode at 830 cm^{-1}. In order to find what kind of oxide it was, an X-ray diagram of this residue was taken using a Debye–Scherrer camera and the micrographs showed that the eight intensities of the reflections (in *Table 2*) are identical to U_3O_8 which have been previously tabulated[7].

CONCLUSIONS

This method has the advantage of being rapid and reproducible when the experimental conditions are carefully controlled.

From the data obtained in *Figure 2* we can propose the possibility for recovery of uranium using this method by direct combustion. This idea is reinforced by the nature of the product, uranium trioxide, which was identified in *Figure 3*. From *Table 1* we can conclude that the polyester residues show a high amount of uranium trioxide. There is a good agreement between the amount of residues found and the maximum capacities of the charged resins. This

Table 1 Residual weight at 600°C, symbols for resins as for those in caption to *Figure 1*

Resins	Uncharged resins (%)	Charged resins (%)	Uranium trioxide (%)
1 (●)	32	43	11
2 (△)	16	40	24
3 (□)	18	60	32
4 (■)	27	62	35
5 (▲)	17	44	27

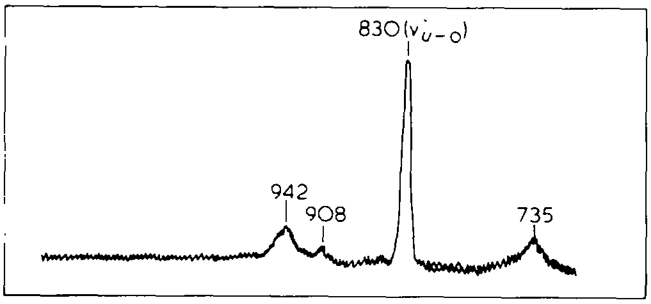

Figure 3 Raman spectra of the residue of phosphorylated polyethylene polyethylene diamine charged with uranium

Table 2 Reflections of uranium oxide

d Å	3.39	1.76	1.94	1.97	1.70	1.28	1.10	1.67
I/I_1	100	80	60	50	50	50	50	10
hkl	100	111	110	110	200	210	301 211	200

method has the advantage of avoiding a step in the procedure, the elution of uranium by salts of acid, with the consequent reduction in the cost of the process.

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REFERENCES

1 Arnold, J. C. *J. Polym. Sci.* 1979, **14**, 267
2 Bartulín, J., Cárdenas, G. and Maturana, H. *Hydrometallurgy* (in press)
3 Clayton, J. O. and Jensen, W. L. *J. Am. Chem. Soc.* 1948, **70**, 3880
4 Arden, T. V. Extr. Refining Rerer Metals, Proc. Symposium, London, 1956, 119-42 (Pub. 1957). C.A., 52, 1980 (1958)
5 Szabó, E., Fodor, A. and Poko, Z. Magyor Tudományos Akad. Központi Fiz. Kutató Intézetének Közleményei. 7, 404–9 (1059). C.A. 54, 16989 (1960)
6 López,, Pérez, B., Uriarte, A., Perarman, M. and Gutiérrez, Jodrá Proc. UN Interm. Conf. Peaceful Uses At. Energy, 2nd, Geneva, 427–43, 1958. C.A. 53, 7898 (1959)
7 X-RAY Powder Data File, Pág. 521, ASTM Special Technical Publication 48-J. American Society For Testing Materials. 1916 Race Street, Philadelphia 3, Pa 1960