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THERMOCHROMATOGRAPHIC ANALYSIS OF INORGANIC FLUORIDE AND OXYFLUORIDE COMPOUNDS

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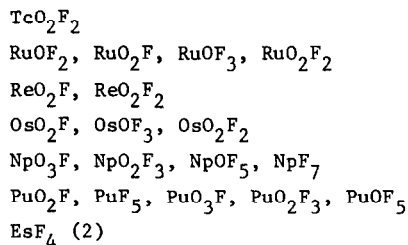
We have developed a new method of chemical analysis of inorganic fluoride compounds of d and f block elements at the tracer scale, in higher oxidation states (\geq IV) (1).

This method, commonly known as thermochromatography, is based upon adsorption and desorption processes of gaseous fluoride compounds, the rate of which depends on the temperature. The apparatus is basically simple, consisting of a fluorinated nickel tube with axial exponential distribution of temperature (850° C to - 150° C). The gas or mixture of gases (HF, HF + O₂, F₂, F₂ + O₂, BF₃ + F₂) react at the hot point of the tube, with an initial deposit of radioelement to form a tagged compound which is carried along the tube, until a point where the temperature is T_c.

Varying the hot point temperature and the gas nature, different compounds of a same element have been obtained. High temperature (800° C) is necessary to form IV and VI oxidation states, while lower temperature (650° C) leads to V and VII oxidation states.

T_c depends on molecular structure of each compound; it means that T_c depends on number and nature of surrounding fluorine or oxygen atoms. It should be noted that T_c is very close for compounds of isostructural configuration (MX_b, MO_aX_b) for different central atom M (see Fig.).

All known fluorides and oxyfluorides were observed for the elements : Tc, Ru, Re, Os, U, Np, Pu, Am, Cm, Bk, Cf. It was possible to detect new gaseous compounds by this method :



Moreover, by this method, separations of Pu-Am or Pu-Cm have been carried out. But an important similarity was observed in the behaviour of Pu and Ru fluorides which inhibits separation of these elements.

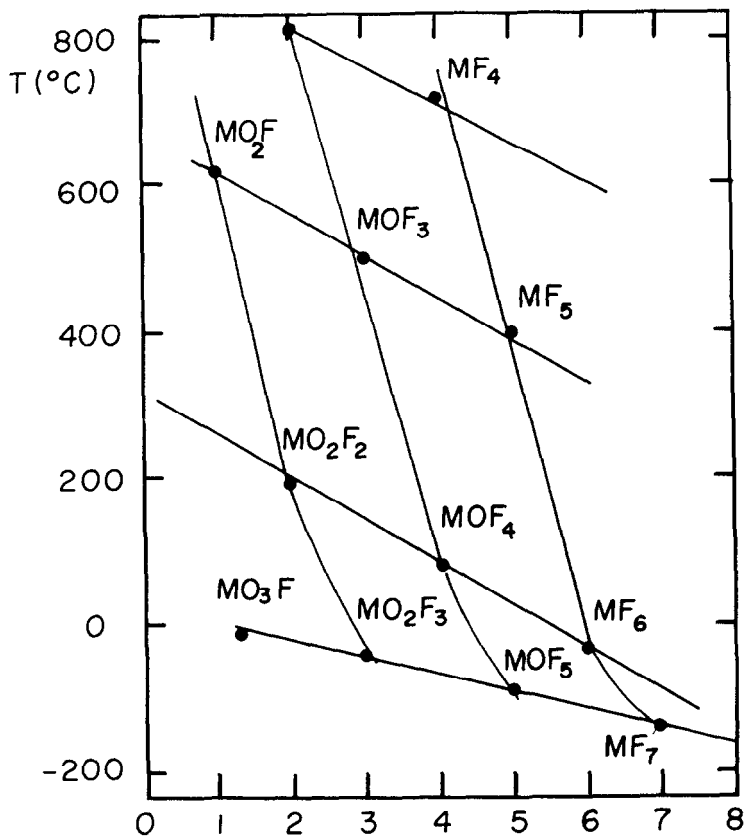


Fig. Number of fluorine atoms

- 1 B. JOUNIAUX, Y. LEGOUX, J. MERINI, G. BOUSSIÈRES, *Radiochem. Radioanal. Letters* 39/2 (1979) 129-140.
M. FARGEAS, Thesis, Orsay, 1986.
- 2 G. BOUSSIÈRES, B. JOUNIAUX, Y. LEGOUX, J. MERINI, F. DAVID, K. SAMHOUN, *Radiochem. Radioanal. Letters* 45/2 (1980) 121-128.