Journal of Fluorine Chemistry, 57 (1992) 73–81

# Electrochemical behaviour of graphite fluoride in aqueous alkaline media

D. Devilliers, H. Groult and M. Chemla
*Université Pierre et Marie Curie, Laboratoire d'Electrochimie, 4 Place Jussieu, 75252 Paris Cedex 05 (France)*

## Abstract

The chemical behaviour of graphite fluoride samples in concentrated alkaline aqueous solutions (5 M) was investigated The kinetics of decomposition obeys Avrami's law. The concentration of liberated $F^-$ ions was determined using a selective fluoride electrode The discharge performances of two $CF_x$ cathodes were compared, for application in $Zn/KOH/CF_x$ batteries In both cases, flat discharge curves were observed, even for high current intensities Values higher than those obtained with conventional 1 M $LiClO_4$–PC electrolytes may be used, because of the higher conductivity of 5 M KOH aqueous solutions

## Introduction

At $350 < T < 600$ °C, fluorine reacts with carbon or graphite, leading to the formation of graphite fluorides, denoted $(CF_x)_n$ or $CF_x$ [1, 2]. The structures of poly(carbon monofluoride), CF, and poly(dicarbon monofluoride), $CF_{0.5}$, are well known. In the formula $CF_x$, $x$ represents the mean stoichiometric coefficient. Lower temperatures (350 °C) favour the formation of $CF_{0.5}$, whereas mainly CF is produced around 600 °C; for intermediate temperatures, a mixture of both graphite fluorides is obtained In fact, the composition of the products also depends on the starting carbonaceous material. Usually, graphitized petroleum coke is used for the manufacture of commercial graphite fluorides.

Fluorine graphite intercalation compounds (GIC) are formed at lower temperatures only if a catalyst is present. For example, $C_x(HF)_yF$, with $2 < x < 5$ is prepared in the presence of HF, and $C_x(MF_z)_yF$ compounds are synthesized in the presence of a metal fluoride $MF_z$ [1, 2].

In spite of their poor electrical conductivity, graphite fluorides are used as cathodic materials in commercial primary lithium batteries. Nonaqueous electrolytes are necessary, for example a solution of lithium perchlorate or tetrafluoroborate in propylene carbonate. However, the working voltage of a $CF_x$/Li cell is considerably lower than the theoretical value, due to a two-step reduction mechanism including the formation

0022-1139/92/$5 00

of an intermediate compound $Li_xCF_x$ and its further decomposition [3, 4]. The presence of a lithium salt in the solution is thought to enhance the performance of the battery because the insertion of $Li^+$ occurs during the discharge process. For example, it has been proved that the reduction of $CF_x$ is easier when $LiClO_4$ is chosen rather than n-$Bu_4NClO_4$ because of the difficult insertion of the bulky cations [5].

Primary batteries using a zinc anode, a $CF_x$ cathode and an aqueous alkaline electrolyte (5-13 M KOH) have been proposed in the patent literature [6]. The discharge curves are flat; the energy density of the $CF_x$ material is comparable with that of $Ag_2O$ or HgO, but its cost is lower Thus the authors claimed that the Zn/$CF_x$ system is suitable for use in miniature-size cells in which HgO cathodes are normally used. The open circuit voltage of the cathode is 1.2 V *vs* a zinc electrode. Since $CF_x$ compounds are hydrophobic, a surfactant is needed in order to ensure the wetting of the $CF_x$ powder by the KOH solution.

More recently, other studies concerning the electrochemical behaviour of $CF_x$ in aqueous alkaline solutions have been reported [7, 8]. The authors have presented discharge curves and X-ray diffraction patterns of the discharge products [7]. XPS spectra of samples treated 5 days in KOH indicated that the $CF_x$ surface is strongly affected by $OH^-$ [8]. In review articles, graphite fluorides are generally described as stable compounds in acidic or alkaline media. However, it is difficult to find reliable quantitative data on the stability of $CF_x$ is such media.

In the present paper, the chemical behaviour of several samples of $CF_x$ in concentrated aqueous alkaline solutions is described. The kinetics of decomposition were determined by measuring the concentration of liberated fluoride ions with a fluoride-selective electrode.

In the second part, the results of electrochemical experiments performed with $CF_x$ cathodes (discharge curves) in aqueous KOH solutions are reported

## Kinetic study

### *Chemicals*

Four samples of commercial graphite fluoride have been tested. one kind of poly(dicarbon monofluoride) (Sample 1) and three kinds of poly-(carbon monofluoride) (Samples 2–4):

— Sample (1): $x = 0.65$ (Cefbon-DM$^R$, Central Glass), prepared from artificial graphite powder (decomposition temperature. $450 < T_d <$ 500 °C).

— Sample (2): $x = 1.1$ (Cefbon-CM$^R$, Central Glass), prepared from petroleum coke. ($400 < T_d < 450$ °C).

— Sample (3)· $x = 1$ 1 (Foracarb$^R$, Atochem).

— Sample (4): $x = 1.13$ (Daikin Industries), prepared from petroleum coke.

A surfactant was used: iso-octylphenoxypolyethoxyethanol, Triton X-100$^{R}$ (Packard). All other reagents were commerical chemicals (Prolabo), used without further purification.

## *Measurements*

The potential of a $M^{z_M\pm}$ ion-selective electrode can be approximately described by the empirical Nernst equation (1), formulated by Nikolsky, in which $a(M)$ is the activity of the measured ion, $a(I_i)$ the activity of the interfering ions, $z_i$ their charge and $k_{M\text{-}I_i}$ the potentiometric selectivity coefficients [9]:

$$E = E^{\circ} \pm (RT/z_M F) \ln\left[ a(M) + \sum k_{M\text{-}I_i}\, a(I_i)^{z_M/z_i} \right] \qquad (1)$$

For the fluoride ion-selective electrode, the main interfering ion is $OH^-$: $k_{F\,OH} = 0.1$. Therefore, it is impossible to detect small concentrations of $F^-$ in concentrated alkaline solutions, and the solutions must be neutralized before measuring the fluoride content.

When the ionic strength is constant, *i.e.* when the same quantity of total ionic strength adjustment buffer (TISAB) is added to each sample, the activity coefficient is constant, the activity $a(F^-)$ is directly proportional to the concentration $(F^-)$, and the response of the electrode *vs* $\log(F^-)$ is linear.

### *TISAB solution*

This solution was prepared for the adjustment of pH and ionic strength. Composition for 1 litre: acetic acid (30 g); sodium acetate (41 g); sodium chloride (58 g); 1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetraacetic acid monohydrate (4 g).

### *Standard NaF solutions; calibration of the electrode*

Each solution contained 1 cm$^3$ of NaOH 5M, 0.4 cm$^3$ of pure $HClO_4$ (for neutralizing NaOH), 20 cm$^3$ of TISAB and the required amount of NaF (aqueous solution, 10 cm$^3$).

E.M.F. measurements were made with a Tacussel Aries 10 000 voltmeter (input impedance $> 10^6$ MΩ). An Orion 94-09 fluoride ion-selective electrode was used as indicator electrode with a Tacussel XR 150 saturated calomel reference electrode. The calibration curve $E = f(F^-)$ was plotted on semilogarithmic paper.

### *Study of the samples:*

In *n* identical tubes containing the same quantity of $CF_x$ ($m = 1.0$ g), two drops of surfactant and 1 cm$^3$ of NaOH 5M were added at $t_0 = 0$. For a given time $t$, 0.4 cm$^3$ of $HClO_4$, 20 cm$^3$ of TISAB and the required quantity of water were added. The study was carried out for times ($t$) ranging from 1 min to 6 or 27 days.

The potential of the electrode immersed in the sample was measured, and ($F^-$) was deduced from the calibration curve. The results may be expressed as a time-dependent function $y(t)$, the ratio of the number of moles of $F^-$ resulting from the decomposition of $CF_x$ to the total number of moles of $F^-$ that would result from the complete decomposition of the compound:

$$y(t) = \frac{n(CF_x)_0 - n(CF_x)_t}{n(CF_x)_0} \tag{2}$$

Longer time ranges have been selected for Sample 4, because this compound was chosen for several electrochemical experiments reported in Section II.

*Results and discussion*

We have used the Avrami–Erofeyev equation (3) in order to analyse the kinetic data:

$$y(t) = 1 - \exp(-kt^n) \tag{3}$$

This law was previously used by Karmarchik and Margrave [10] and by Koyama [11] for analyzing the kinetics of thermal decomposition of $CF_x$ in vacuum. For most samples, the value of $n$ was found to be $\simeq 2$.

An equation solver (Eureka software, Borland) was used to fit experimental data. The Avrami equation is obeyed and the best value of $n$ was found to be $n = 0.75$ for all the samples; the value of the rate constant $k$ is reported in Table 1. Its value is in the range $1–5 \times 10^{-4}$ $h^{-n}$, where $n = 0.75$. Decreasing values of $k$ were obtained for increasing values of the stoichiometric coefficient $x$ of $CF_x$.

Figure 1 shows the experimental points and the theoretical curves, according to eqn. (3), and using the values of $n$ and $k$ determined with the Eureka software for Samples 1, 2 and 3. Figure 2 shows the data for Sample 4, which was studied on a longer time scale. The best behaviour is observed for Sample 1 ($CF_{0.65}$).

It is clear that the graphite fluorides generally do not exhibit very good stability in aqueous alkaline solutions in the presence of the surfactant reported above: first, the $CF_x$ samples turned from white to black after several days immersion in the alkaline media; second, the analysis of

TABLE 1

Kinetic constant, $k$, for the decomposition of graphite fluoride samples in 5 M KOH solutions

| Sample | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Time range (h) | 145 | 145 | 145 | 650 |
| $k \times 10^4$ ($h^{-n}$) | 1.02 | 5.4 | 4.2 | 2.9 |

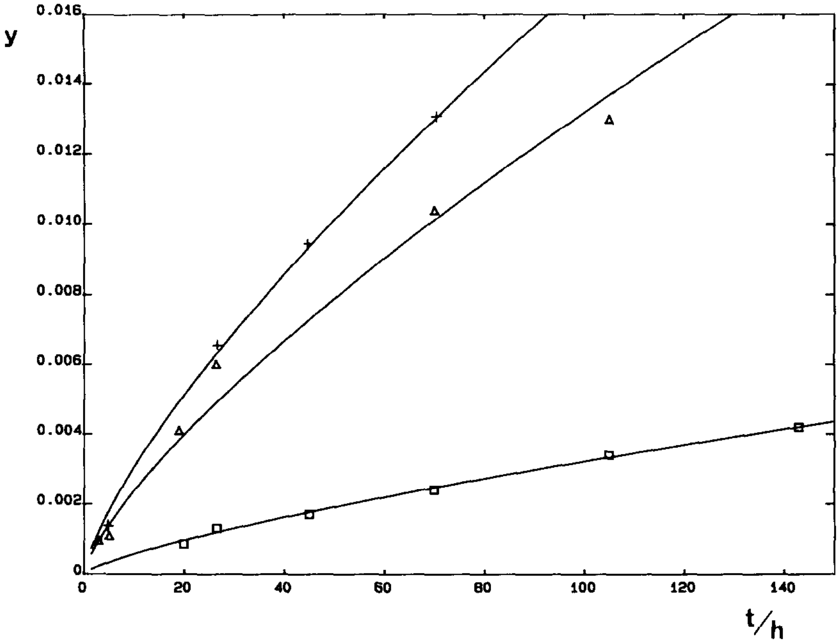

Fig 1 Decomposed fraction $y$ of graphite fluoride samples in 5 M KOH solutions *vs* time Calculated values continuous curves, experimental data: Sample 1 ($CF_{0.65}$) (□), Sample 2 ($CF_{1.1}$) (+), Sample 3 ($CF_{1.1}$) (△)

the $F^-$ concentration in the solutions proved that the percentage of decomposition of $CF_{1.13}$ is roughly 1% after about 5 days immersion. These quantitative results are in agreement with several qualitative results reported previously in the literature: a change with time of the spontaneous potential of the $CF_x$ electrode in KOH solutions (9 M) and evolution of XPS spectra after immersion in KOH for 5 days [8]. As the stoichiometry at the interface is modified due to the rupture of C–F bonds, the rest-potential and the spectra are also modified.

## Electrochemical behaviour

For these experiments, the carbon paste electrode technique was used, which allows the study of insoluble and insulating compounds drowned in a conductive carbon paste [12, 13].

### *Chemicals; electrochemical apparatus*

$CF_{1.1}$, denoted Sample 2, and $CF_{1.13}$, denoted Sample 4, were used. 5 M alkaline aqueous solutions were prepared with potassium hydroxide R. P. Prolabo. A surfactant, Triton X-100® Packard (iso-octylphenoxypolyethoxyethanol) was added to the carbon paste.

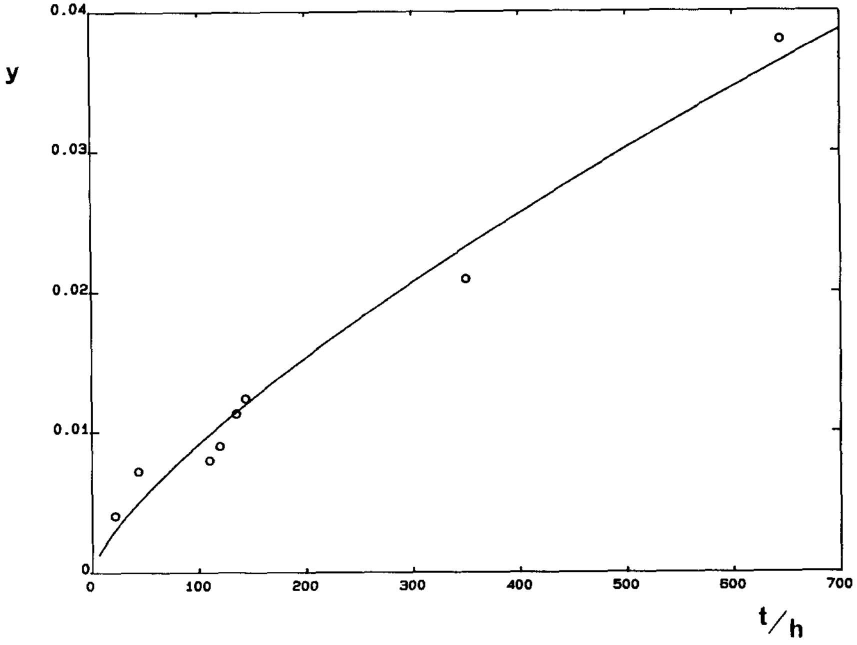

Fig 2 Decomposed fraction $y$ of $CF_{1.13}$ (Sample 4) in 5 M KOH solutions *vs* time Calculated values continuous curves, experimental data circles

The experiments were carried out at room temperature in the polypropylene cell described in [5], fitted with a carbon paste working electrode, an auxiliary platinum electrode, and a Hg,HgO reference electrode containing 1 M KOH solution. This electrode was separated from the main compartment of the cell by a glass-frit.

The carbon paste was a mixture of $CF_x$ (0.03 g) and Johnson Matthey non-pelletable graphite powder (0.09 g) wetted with a few drops of the electrolytic solution and surfactant. Galvanostatic experiments were performed, using a PRT 10*0.5 Tacussel electrochemical device. The resulting discharge curves were plotted on a recorder.

As it is reported that high utilization of the cathode material is achieved only if fine particles of $CF_x$ powder are used [6], it was necessary to measure the average size of the $CF_x$ crystallites and their specific area.

Sample 4 was examined with a Jeol JEM CX II electron microscope equipped with a Jeol scanning attachment STEM-SEM. It exhibits a layered structure, with average size of the layers 5 × 12 μm.

Its specific area was deduced from nitrogen adsorption experiments (BET method): $S = 285 \pm 5\ m^2\ g^{-1}$. This value is acceptable for battery application because it is reported that the best results are obtained for $CF_x$ for which the specific area is greater than $200\ m^2/g$ [6].

*Results and discussion*

Hereafter, all potentials are referred to the Hg,HgO/1 M KOH electrode.

Figure 3 presents the discharge curves obtained with Sample 4 for $i = 1$ mA and $i = 2$ mA. Other experiments, for $i = 0.5$ mA and $i = 1$ mA, are reported in Fig. 4. For these last two experiments, several interruptions were made, and it can be seen that flatter discharge curves were obtained. The average open circuit voltage (OCV) was $-(0.05 \pm 0.01)$ V, corresponding to the following overvoltages: $\eta = 0.45$ V for $i = 1$ mA, $\eta = 0.35$ V for $i = 0.5$ mA. Comparable values are reported in the literature: $\eta = 0.39$ V for $i = 1$ mA [6].

The results obtained with Samples 2 ($CF_{1.1}$) and 4 ($CF_{1.13}$) are reported in Table 2. The discharge performance of graphite fluorides may be compared from the discharge yield, $r$, which is the ratio of the experimental capacity, $Q_{exp}$, to the theoretical capacity, $Q_t$ (905 mA h g$^{-1}$ for $CF_{1.13}$, and 896 mA h g$^{-1}$ for $CF_{1.1}$). Even for large intensities, the value of $r$ is always larger than that obtained with 1 M $LiClO_4$–PC electrolytes, using exactly the same cell configuration. If discharges are performed with large intensities, using the latter electrolyte, very low values of $r$ are obtained. For example: $i = 1$ mA, $r = 0.30$ with Sample 4.

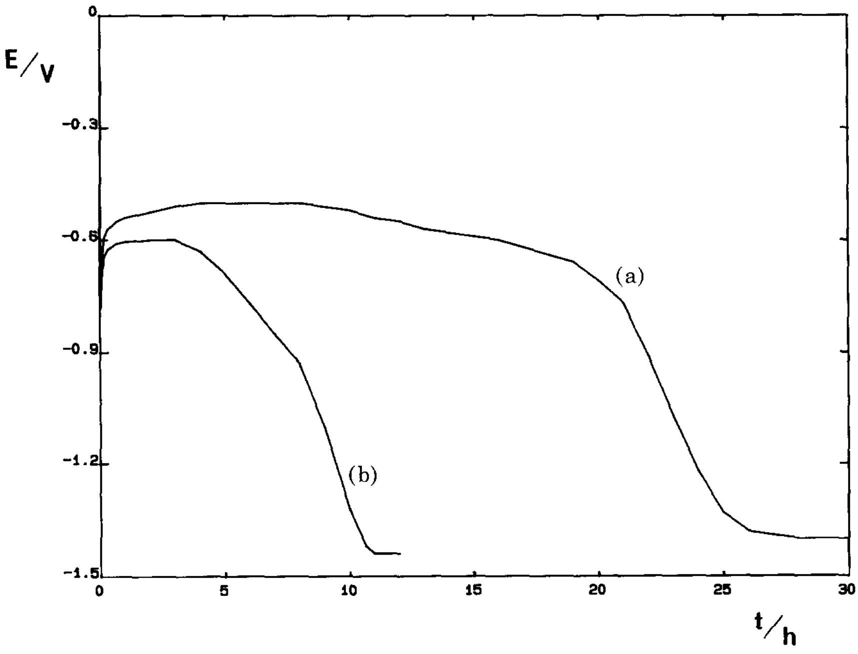

Fig 3. Galvanostatic discharge curves performed with Sample 4 ($CF_{1.13}$) in 5 M KOH solutions. (a) $i = 1$ mA, (b) $i = 2$ mA.

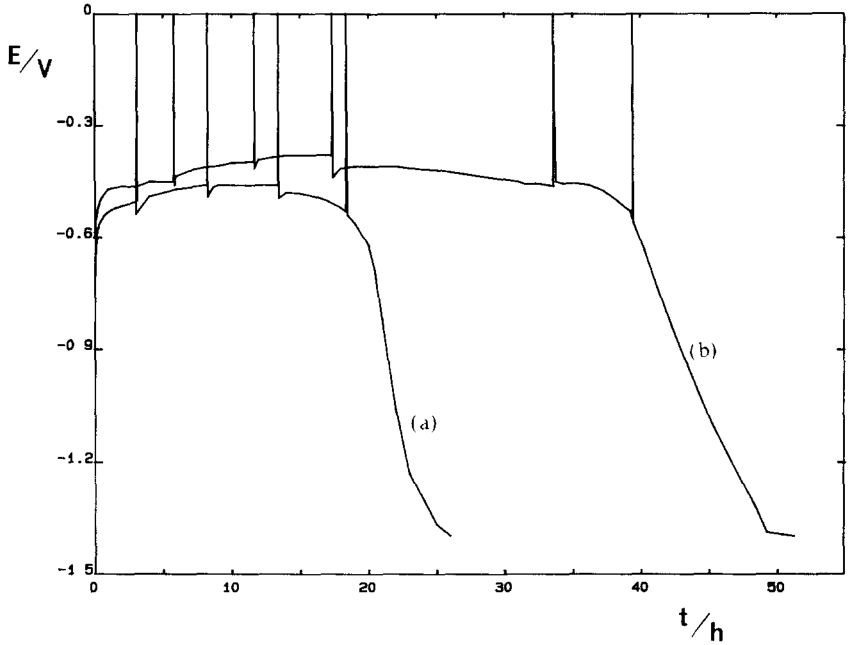

Fig 4 Galvanostatic discharge curves performed with Sample 4 ($\mathrm{CF}_{1\ 13}$) in 5 M KOH solutions (a) $i = 0\ 5$ mA, 70-h interruptions, (b) $i = 1$ mA, 18-h interruptions

Zn/KOH/$\mathrm{CF}_x$ batteries present most of the properties which are required for a practical primary battery: flat discharge potential, large capacity and high utility of the active mass

However, in commercial batteries, $r$ would be somewhat lower than 1 because of the chemical decomposition of the $\mathrm{CF}_x$ sample in contact with the alkaline solution in the presence of a surfactant. Therefore, care must

TABLE 2

Duration of the galvanostatic discharge, $t_{\mathrm{exp}}$, and yield, $r$, for $\mathrm{CF}_x$ samples in aqueous 5 M KOH solutions

| $I$ (mA) | Sample (2) $\mathrm{CF}_{1\ 1}$ | | Sample (4) $\mathrm{CF}_{1\ 13}$ | |
|---|---|---|---|---|
| | $t_{\mathrm{exp}}$ (h) | $r$ | $t_{\mathrm{exp}}$ (h) | $r$ |
| 0 5 | 31 | 0 58 | 42 5 | 0 78 |
| | | | 39 5[b] | 0 73 |
| 1 | 13 5 | 0 50 | 21 | 0 77 |
| | 16[a] | 0 60 | 20[a] | 0 74 |
| 2 | 7 3 | 0 54 | 8 3 | 0 61 |

[a] Results obtained with several 18-hour interruptions
[b] Results obtained with several 70-hour interruptions

be taken in the choice of the latter in order to avoid a loss of capacity. For example, the results above show that 4% of the $CF_{1.13}$ may be decomposed after one month storage.

Nevertheless, some performances are better than those obtained with non-aqueous solutions because the conductivity of KOH is much higher (for example: $\kappa = 7.13 \times 10^{-3}$ S cm$^{-1}$ for 1 M $LiClO_4$ in propylene carbonate and $\kappa = 0.57$ S cm$^{-1}$ for 5 M KOH). Therefore, Zn/$CF_x$ batteries with concentrated solutions of KOH can discharge with a flat potential response even at high current intensities. These batteries do present interesting features that allow their use instead of HgO–cathode batteries.

## Acknowledgements

The authors would like to thank Mrs P. Beaunier, Service de Microscopie Electronique, Université Pierre et Marie Curie, who performed the scanning electron microscopy experiments, and Mr. J. L. Bonardet, Laboratoire de Chimie des Surfaces, Université Pierre et Marie Curie, who determined the specific area of the sample by the BET method.

## References

1 T Nakajima and N Watanabe, *Graphite Fluorides and Carbon-Fluorine Compounds*, CRC Press, Boca Raton, FL, 1991, p 123

2 N. Watanabe, T Nakajima and H Touhara, *Graphite Fluorides*, Elsevier, Amsterdam, 1988, p 240

3 M S. Whittingham, *J Electrochem. Soc*, *122* (1975) 526

4 N. Watanabe, R Hagiwara and T Nakajima, *J Electrochem Soc*, *131* (1984) 1980

5 D. Devilliers, B. Teisseyre, M. Chemla, N Watanabe and T Nakajima, *J Fluorine Chem*, *40* (1988) 1

6 *U S Pat 3 956 018* (1976) to Union Carbide Corp (A Kozawa)

7 K Horita and T Shimizu, *Nippon Kagaku Kaishi*, (1984) 1227

8 K Horita, M Nishikawa and K Kawakami, *Nippon Kagaku Kaishi*, (1987) 2231

9 K Cammann, *Working with Ion-Selective Electrodes*, Springer Verlag, Berlin, 1979, p 29

10 P Kamarchik Jr and J L Margrave, *J Thermal Anal*, *11* (1977) 259.

11 S. Koyama, *Thesis*, Kyoto, 1980.

12 R N Adams, *Anal. Chem*, *30* (1958) 1576

13 T Kuwana and W G French, *Anal Chem*, *36* (1964) 241