

# THE QUANTITATIVE SEPARATION OF PERIODATE AND IODATE BY THIN-LAYER ELECTROPHORESIS ON STRIPS OF PLASTER OF PARIS

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Electrophoretic separation of inorganic anions on paper has found applications in analytical as well as radiochemical problems and, while paper electrophoresis has been employed<sup>1-5</sup> for the separation of periodate and iodate, this method has not proved satisfactory. Two or more spots have been observed on some papers<sup>2,4</sup> and Whatman No. 3MM has been suggested to be superior to other papers<sup>5</sup>. Since periodate is a strong oxidising agent in an acid as well as an alkaline medium and since it also forms complexes with polyhydroxy compounds (such as cellulose) which are believed to be the first stage of the reduction reaction, we considered cellulose *a priori* unsatisfactory for quantitative and trace scale separations of periodate and iodate. The reaction of complex formation is a suspected cause of the multiple spots observed and the reduction reaction a cause of the reduction comet which has been observed in several separations<sup>6</sup>.

In this paper we shall describe the investigation of inorganic supports to replace cellulose in paper electrophoresis. Preliminary work with Whatman glass fibre paper gave indifferent results, yielding with periodate, amongst others, a cationic spot which oxidised acid potassium iodide. Glass fibre paper was therefore not further studied. Plaster of Paris in thin layers on glass plates was then tried, as it had been found satisfactory for several chromatographic separations<sup>7</sup>. It was noted that periodate gave one single spot at the start when chromatographed with 0.05M ammonium carbonate and that iodate moved as a diffuse trail close to the liquid front. Sodium hydroxide in various concentrations (1 N, 0.1 N and 0.01 N) was also tried but was found to attack the plaster of Paris strips. During electrophoresis on plaster of Paris, iodate moves as a compact spot and is readily separated from periodate, which forms one single spot at the point of origin.

In the experimental part below we were able to show that it is possible to separate macro amounts quantitatively on plaster of Paris and that trace amounts, produced by neutron irradiation of potassium periodate (Szilard-Chalmers reaction), gave considerably increased yield by comparison with electrophoretic separations on paper run parallel to the separation on plaster of Paris.

## EXPERIMENTAL

### (a) Preparation of thin layers of plaster of Paris

It is important to control the purity of the plaster of Paris used. Some samples gave a

blue colour with starch-iodide and had to be rejected. Commercial plaster of Paris (supplied by Hopkins and Williams) gave the best results of the various products tried.

About 25 g were stirred with 30 ml of distilled water and after about 3 min poured into a mould made of glass plates as shown in Fig. 1; another glass plate was then

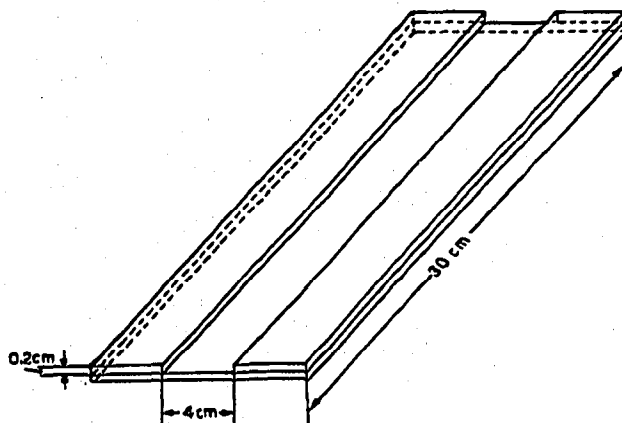


Fig. 1. Arrangement of glass slides to form the mould for the preparation of the thin layers.

placed over this and the whole left about 48 h in an oven at 60°. Thin glass plates (about 1 mm thick) are recommended for radioactive substances to avoid self-shielding.

#### (b) *Electrophoretic separation*

The Jouan apparatus for paper electrophoresis was used to support the thin layers. Contact between the electrode vessels and the horizontally placed layer was made with two pieces of Whatman No. 1 paper. As electrolyte, 0.05M ammonium carbonate was employed throughout and was sprayed onto the thin layer to saturation. For quantitative work thin layers without glass support were found to have sufficient rigidity if supported by two glass rods at the sides. The volume of solution to be analysed was placed on the strip moistened with the electrolyte by means of an Agla syringe. Samples of 0.05 ml were usually applied and these were placed in the previously pencil-marked centre.

Potentials of 300 to 400 V for 1.5 to 2 h (with 5 to 10 milliamps) gave complete separation of iodate from periodate. Radioactivity measurements along the thin layers were carried out with the counter described by LINSKENS<sup>11</sup>.

#### (c) *Quantitative analysis*

The portions of the thin layer containing the periodate and the iodate were placed in glass-stoppered Erlenmeyer flasks, broken up and titrated with  $N/100$  thiosulphate, after addition of excess acid and potassium iodide, to a starch end-point. Since we did not trust the stability of aqueous solutions of periodate and iodate, aliquots of the solution to be placed on the thin layer were also analysed each day by titrating the periodate with  $N/100$  arsenite in alkaline solution and the sum of periodate and iodate with thiosulphate in acid solution on a separate sample<sup>10</sup>. Table I gives the

results obtained before and after electrophoretic separation. Only quantities of the order of 1 mg can be analysed by this method owing to the low solubility of potassium periodate in aqueous solutions.

TABLE I  
QUANTITATIVE ANALYSIS OF MACRO AMOUNTS OF PERIODATE AND IODATE

Periodate (mg) present	Periodate (mg) found	Iodate (mg) present	Iodate (mg) found
0.30	0.30	1.10	1.14
0.86	0.86	1.58	1.56
0.36	0.36	0.27	0.27
1.06	1.08	2.48	2.54
0.47	0.47	0.69	0.65
0.19	0.19	1.36	1.36
1.06	1.12	2.48	2.40
0.47	0.48	0.67	0.67
0.21	0.21	1.26	1.24
0.12	0.12	0.23	0.24
0.36	0.36	0.25	0.25
0.30	0.30	1.10	1.13

(d) Separation of radioactive periodate and iodate

Samples of potassium periodate were irradiated for 1 h in a Triga swimming pool reactor in a flux of about  $10^{12}$  neutrons/cm<sup>2</sup>/sec. Annealing was then carried out on some samples for 15 min at 240°. The results obtained by electrophoresis on plaster of Paris indicate that about 80 % of radioactive periodate and 20 % of iodate are so formed and this agrees well with the findings of ATEN *et al.*<sup>8</sup>. A typical separation is shown in Fig. 2. A parallel separation carried out on cellulose paper is shown in Fig. 3 and shows that the periodate peak is considerably lower, presumably due to reduction.

Separations on plaster of Paris and paper of irradiated samples which were not annealed are shown in Figs. 4 and 5 and again the amount of periodate found on paper is considerably lower than that on plaster of Paris. These experiments were repeated several times and parallel separations on paper were carried out. The relative percentages of periodate and iodate are shown in Tables II and III.

TABLE II

Experiment	% Activity due to $KIO_3$ irradiated without annealing. Electrophoresis on:	
	Plaster of Paris strip	Whatman 3MM paper
1	12	3
2	10	1.8
3	12	2
4	9	2.7
5	8.7	2.8
6	10	2.9
7	13	2

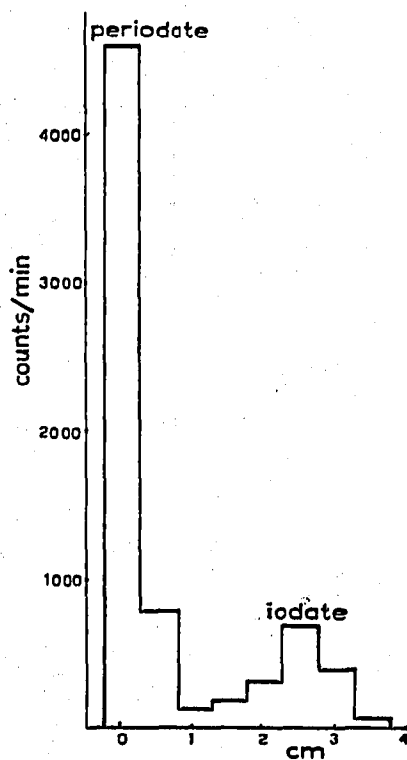


Fig. 2. Separation of radioactive  $K^{128}IO_4$  and  $K^{128}IO_3$  as formed by irradiation and subsequent annealing. Separation on a thin layer of plaster of Paris with 400 V for 1.5 h with 0.05 M ammonium carbonate as electrolyte.

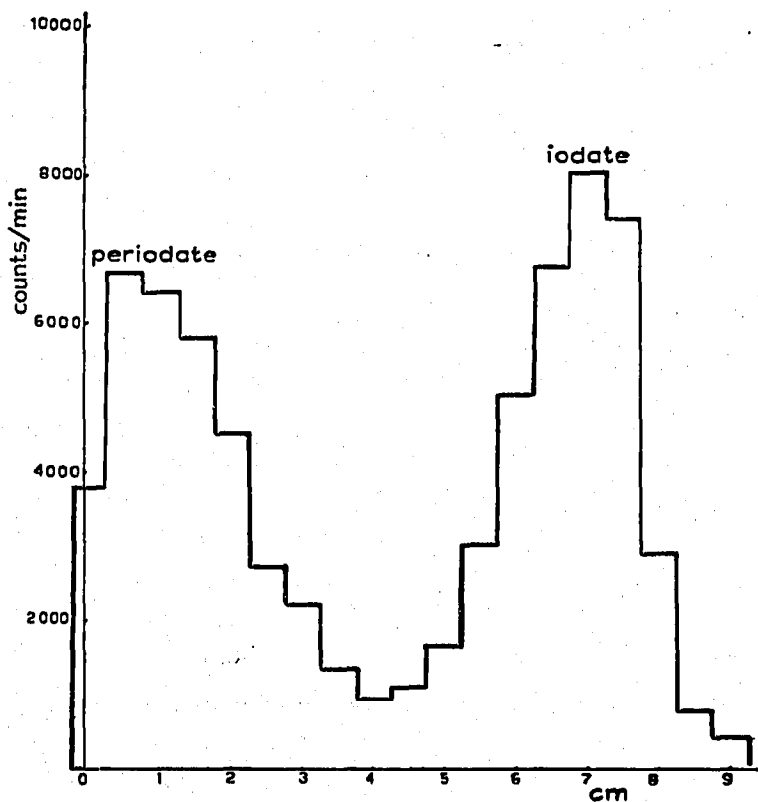


Fig. 3. As in Fig. 2 using Whatman No. 3 MM paper as support for the separation instead of plaster of Paris.

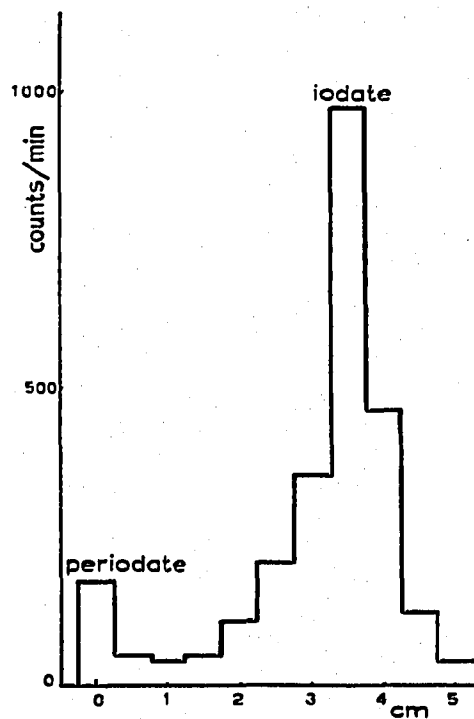


Fig. 4. As in Fig. 2 without annealing. Separation on plaster of Paris with 400 V for 2 h.

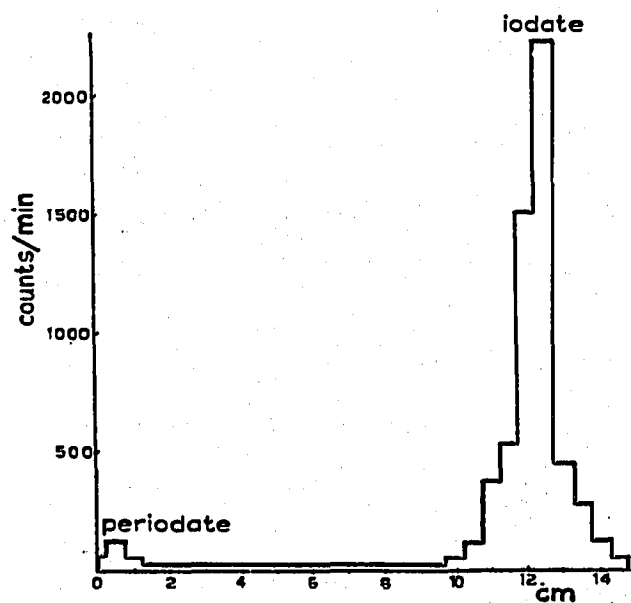


Fig. 5. As in Fig. 4 on Whatman No. 3 MM paper instead of plaster of Paris.

The values for samples without annealing agree with the findings of CLEARY *et al.*<sup>9</sup> It would thus seem that, under the usual conditions for paper electrophoresis, considerable amounts of trace periodate are converted to iodate.

TABLE III

Experiment	% Activity due to $KIO_4$ irradiated and annealed at 240° for 15 min. Electrophoresis on:	
	Plaster of Paris strip	Whatman 3MM paper
1	85	48
2	79	37
3	81	44
4	80	45
5	85	39

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## SUMMARY

The electrophoretic separation of periodate and iodate was carried out on thin layers of plaster of Paris with 0.05 *M* ammonium carbonate as electrolyte with 300–400 V for 1.5 to 2 h. Quantitative separations of milligram amounts and separation of trace amounts are reported.

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