

## Paper partition chromatography of mixtures of chloride, chlorite, chlorate and perchlorate

Chloride ion and several inorganic species containing chlorine and oxygen are capable of coexistence in the pH range 3–11, but also undergo interconversions, either by interaction with each other or with other inorganic or organic materials present in the aqueous solution<sup>1–5</sup>. The complexity of such reactions has made facile identification of the various species highly desirable. Detection of chlorine dioxide is no problem, since it is highly volatile and absorbs in the near ultraviolet<sup>6</sup>. A method for identifying the remaining (anionic) species was sought, however. Separation of chlorate from chlorite on paper chromatograms had been achieved by SERVIGNE<sup>7</sup> and by LAUB<sup>8</sup>, but neither achieved a good separation of chloride; LAUB was unable to keep hypochlorite ion stable in the solvent system used by him, and in this regard we were also unsuccessful. The separation of chloride from chlorite achieved in the present work is of particular significance, since the heavy metal salts of both these ions have similar solubilities, making precipitation tests with compounds of these metals uncertain at best. At the same time, it has also been possible to improve the detection sprays used by the previous authors, both with regard to ease of handling and to sensitivity.

### Procedure

Strips of Whatman No. 1 filter paper measuring 5 × 43 cm were spotted 4 cm from one end with various mixtures made from 1% solutions of sodium chloride, sodium chlorite, sodium perchlorate and potassium chlorate and permitted to dry. At least 10  $\mu\text{g}$  of each anion was applied. Each strip was then developed for about 16 h\* in a "Chromatobox" (Model A-801, obtainable from the Emil Greiner Company, 20 N. Moore St., New York 13, N. Y.) with a 15:2:2:2 mixture of 2-propanol, water, pyridine and concentrated ammonium hydroxide, and dried at room temperature. The portion of the strip up to 11 cm from the starting line was sprayed with 0.2 *N* aqueous silver nitrate while the remainder of the strip was shielded from the spray; after drying, the strip was exposed for 2 min to an ultraviolet lamp, which caused a dark purple spot, due to chloride ion, to appear at  $R_F$   $0.25 \pm 0.02$  (center of spot). Tannish streaks due to hydroxides of sodium and potassium appeared at  $R_F$  0.09–0.12; the presence of these hydroxides was evidently due to the separation of the salts originally applied into fast-moving anions and slow-moving cations, the latter acquiring hydroxyl from the solvent as their counter ion. The region from 11 cm to 24 cm was sprayed with a fresh mixture of equal parts of 3 *M* aqueous hydrochloric acid–acetone (1:1) and 5% ethanolic diphenylamine; this revealed chlorite immediately as a blue spot,  $R_F$   $0.36 \pm 0.02$ , and chlorate, after drying 2–3 min, as a green spot of  $R_F$   $0.54 \pm 0.02$ . The remainder of the strip was sprayed with saturated aqueous sodium acetate, dried, and oversprayed with 0.2% aqueous methylene blue to locate perchlorate as a violet spot of  $R_F$   $0.71 \pm 0.02$  against a light blue background. There was no difficulty in detecting as little as 10  $\mu\text{g}$  of each anion.

Experiments of the type described above showed that hypochlorite ion, stable for a short time as a dried spot on filter paper, decomposes on exposure to the solvent

\* Good chromatograms can be obtained in even 4 h, in which case the  $R_F$  values are 0.25, 0.34, 0.50 and 0.65 for the four ions.

mixture. Without chromatographing, the dried spot could be visualized as a brown spot by spraying with iodide buffered with carbonate-bicarbonate; under these conditions the other oxy-chloro anions are unreactive.

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### Use of 2-(*o*-hydroxyphenyl)-benzoxazole in detection of phosphate esters and other ferric-complexing compounds on paper chromatograms

Spots of phosphate esters on paper chromatograms are usually detected by the method of HANES AND ISHERWOOD<sup>1</sup> or one of its modifications, involving hydrolysis to inorganic phosphate, reaction with molybdate and reduction to molybdenum blue. This is sensitive to about 1 nanomole (0.03  $\mu\text{g}$ ) of P but is relatively slow and inconvenient to use. WADE AND MORGAN<sup>2</sup> introduced a detection based on the masking of the color reaction between ferric ions and sulfosalicylic acid. This method is less specific and is sensitive only to 30 nanomoles of P, but it is fast and does not destroy the compounds being detected. We have found that the fluorescent compound, 2-(*o*-hydroxyphenyl)-benzoxazole, which reacts with many metallic ions<sup>3</sup>, can be used instead of sulfosalicylic acid. The benzoxazole fluorescence reaction requires only very low reagent concentrations, it is somewhat more sensitive, and works well over a wide pH range (while the sulfosalicylic color requires a pH near 2).

Reagent PD-1A is a 0.54 % solution of  $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$  in 80 % (v/v) ethanol and is stable for months. Before use, a 1:50 dilution in acetone (reagent PD-1B, approximately 0.0004 *M* ferric ion) is prepared. It is applied to the paper with a pipet, in quantity just sufficient to saturate it. The paper is allowed to dry for a few minutes, and then reagent PD-1C, a 0.05 % (0.0024 *M*) solution of 2-(*o*-hydroxyphenyl)-benzoxazole and 2 % (v/v) dimethyl sulfoxide in 2-butanone is applied with a pipet. This kind of application is more convenient than spraying or dipping and gives a more uniform deposit of reagents. When the paper is examined in long-wave ultraviolet light, spots of ferric-complexing compounds fluoresce yellow (if the paper is acidic) or