Paper chromatography of Sn²⁺ and Sb³⁺

Sn²⁺ and Sb³⁺ are rather difficult to separate by paper chromatography[1] and very few good separations[2] of these cations have been reported. The separations obtained by HARASAWA[3] and STEFANOVIĆ et al.[4] could not be confirmed by LEDERER[1] or by us. The paper chromatography of these cations was therefore studied more exhaustively. As a result some good separations have been developed.

Some of the solvents tried were: propionic acid, butyric acid, isovaleric acid, palmitoyl chloride, acetyl chloride, acetic anhydride, aniline, diethylamine, methyl-cyclohexanone, anisole, aliphatic alcohols, acetaldehyde, formaldehyde, quinoline,

TABLE I

ASCENDING CHROMATOGRAPHY

	Solvent	R_F		Time h
		Sn^{2+}	Sb^{3+}	
1	*Formic acid–anisole (1:1)	0.26	0.54	2
2	Formic acid–anisole (1:2)	0.14	0.44	2
3	Acetic acid–formic acid (1:1)	0.33	0.47	2
4	Acetic acid–formic acid (1:2)	0.42	0.53	2
5	Formic acid–butyric acid (1:1)	0.36	0.52	2
6	Formic acid–propionic acid (1:1)	0.19	0.41	2
7	Formic acid–propionic acid (1:2)	0.16	0.40	2

TABLE II

DESCENDING CHROMATOGRAPHY

	Solvent	R_F		Time h
		Sn^{2+}	Sb^{2+}	
1	*Formic acid–anisole (1:1)	0.14	0.50	2
2	Acetic acid–formic acid (1:2)	0.39	0.47	2
3	Formic acid–butyric acid (1:1)	0.31	0.46	2
4	Formic acid–propionic acid (1:1)	0.33	0.48	2

TABLE III

CIRCULAR CHROMATOGRAPHY

	Solvent	R_R		Time min
		Sn^{2+}	Sb^{3+}	
1	*Formic acid–anisole (1:1)	0.39	0.67	20
2	Acetic acid–formic acid (1:2)	0.51	0.67	20
3	Formic acid–butyric acid (1:1)	0.33	0.53	20
4	Formic acid–propionic acid (1:1)	0.36	0.62	20

2,4-hexanedione, lactic acid and 10 % solutions of urea, thiourea, succinic acid, tartaric acid, citric acid, ammonium chloride, sodium chloride, potassium chloride and sodium bisulphite.

Papers impregnated with the following organic and inorganic adsorbents were also used: ammonium oxalate, ammonium carbonate, glucose, naphthalene, benzoic acid and sodium chloride.

The successful separations are given in Tables I, II and III. The systems that gave the best results are marked with an asterisk.

In order to find out whether the separations can be of use in qualitative analysis $M/5$ test solutions of $SnCl_2$ and $SbCl_3$ were mixed in different ratios and separated by ascending chromatography using a mixture of anisole and formic acid ($1:1$) as the developer. In all cases good separations were obtained. The papers were conditioned for 1 hour prior to chromatography. The results are summarized in Table IV.

TABLE IV

SEPARATION OF MIXTURES OF Sn^{2+} AND Sb^{3+} OF VARYING COMPOSITION

Ratio of $SnCl_2:SbCl_3$	R_F		Time of development h
	Sn^{2+}	Sb^{3+}	
2 : 1	0.18	0.52	1
3 : 1	0.19	0.51	1
4 : 1	0.22	0.53	1
1 : 2	0.10	0.48	1
1 : 3	0.17	0.61	1
1 : 4	0.17	0.52	1

The test solutions were diluted to $M/50$ and $M/100$. When these solutions were spotted and developed with anisole–formic acid ($1:1$), after conditioning for one hour, good separations were obtained. The results are summarised in Table V.

TABLE V

SEPARATION OF Sn^{2+} AND Sb^{3+} AT HIGHER DILUTIONS (ASCENDING TECHNIQUE)

Concn. of test solution	R_F		Time of development h
	Sn^{2+}	Sb^{3+}	
$M/50$	0.06	0.38	1
$M/100$	0.01	0.36	1

The zones of Sn^{2+} were always compact, well defined and well separated, while the zones of Sb^{3+} were sometimes a little diffuse.

On repeating the separation reported by STEFANOVIĆ et al.[4] it was found that besides being time-consuming (21 hours) their method is not reproducible. Similarly the separation advocated by HARASAWA[3] fails under the conditions specified. It is possible that in our separations formic acid plays a beneficial role by preventing the oxidation of Sn^{2+} and Sb^{3+} to higher valence states.

Butyric acid commercial 50% (E. Merck) and anisole, free from alcohol (Naarden), were used. All the other chemicals were of reagent grade, either from E. Merck, or British Drug Houses. Schleicher & Schüll No. 2043a sheets were used for ascending and descending chromatography. Whatman No. 1 filter paper circles (diameter 12.5

cm) were used with the Kawerau apparatus. The $M/5$ test solutions of $SnCl_2$ and $SbCl_3$ for the experiments given in Tables I–IV were prepared as follows:

1.89 g of $SnCl_2$ and 2.28 g of $SbCl_3$ crystals were dissolved in 15 ml of conc. HCl separately and the solutions were then diluted to 50 ml with distilled water. The $M/50$ and $M/100$ test solutions were prepared by subsequent dilution with 30% HCl. Two spots (approx. 0.0014 ml) of each of the two test solutions were applied to the test paper with a thin glass capillary. The cations were detected by hydrogen sulphide gas. The room temperature was 26° $\pm$ 4°.

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A simple apparatus for keeping the final pressure in gas chromatographs constant

In the chromatographic analysis of gases with the aid of katharometer detectors both the peak height and the retention time depend on the flow rate of the carrier gas; the peak height moreover depends on the pressure in the detector cell. The factors which affect the flow rate of the gas are the pressure before the column, the resistance of the column, and the pressure after the column. The pressure before the column and the resistance of the column can be easily kept constant by using suitable regulating valves and by thermostating the column. The pressure after the column, however, depends on the barometric height. In serial tests, in which the calibration curve is not checked after each measurement, the change in barometric height over a few hours or days may cause considerable deviations from the calibration curve; according to our experience, the peak height varies by about 0.1% upon 1 mm change in barometric height. A diagram of a simple apparatus for keeping the pressure after the column constant is shown in Fig. 1.

The exit of the detector cell 1 is provided with a needle valve 2. A differential pressure gauge 3, which measures the pressure difference between the points 1 and 4, is fitted between the cell and the valve. 4 is a glass bulb with a capacity of approx.