

Das beschriebene Verfahren der gravimetrischen Einstellung der Gemische hat gegenüber der vielfach üblichen volumetrischen Herstellung von Eichgemischen ausser der genaueren Messung den Vorteil, dass bei Vorliegen von Dampf- und Flüssigphase in den Stahlgefässen (Probeflasche C nach DIN 51 610) nebeneinander durch einfaches intensives Schütteln schnell eine homogene Mischung erhalten werden kann.

Die angegebenen Füllmengen von bis zu 40 g erscheinen für die meisten Laboratorien angemessen und reichen sogar in den meisten Fällen als Eichgemisch über einen grösseren Zeitraum. Sie können ohne Bedenken gelagert werden, wenn sich die Gemische in V2A- bzw. V4A-Stahlgefässen befinden.

Das angegebene Verfahren hat sich als geeignete Methode im Falle von Analysenvergleichen zwischen verschiedenen Laboratorien bewährt und lässt sich ausser auf Gaschromatographiegeräte auch auf andere physikalische Gasanalysengeräte, wie z.B. Spektrometriegeräte, anwenden.

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<sup>1</sup> W. J. BAKER UND T. L. ZINN, "Preparation of Gas Calibration Samples", *Perkin-Elmer Instr. News for Science and Industry*, S. 1, 8.

<sup>2</sup> F. VAN DE CRAATS, in D. H. DESTY, *Gas Chromatography 1958*, Proc. 2nd Symposium Amsterdam, May 1958, Butterworths Sci. Publ., London, 1958, S. 248.

Eingegangen den 5. Oktober 1962

*J. Chromatog.*, 11 (1963) 120-122

### Electromigration in fused salts in the study of complex ions

The existence of complex ions in molten salt solutions has frequently been postulated, and direct evidence is available in a number of cases. Paper electromigration can be used to determine the sign of the charge on an ion, and is a particularly simple way of proving that anionic complexes of metal ions exist in solution. Electromigration in asbestos or glass fiber paper with a fused salt as background electrolyte has been described by ARNIKAR<sup>1</sup> and by ALBERTI *et al.*<sup>2</sup> We have used this technique to show the presence of a number of transition-metal thiocyanate complexes in solution in molten KCNS, and to compare the behavior of these metals here with that in molten LiNO<sub>3</sub>-KNO<sub>3</sub> eutectic mixture where essentially no complexing is expected.

The electromigration was carried out in strips of Whatman GF/A glass fiber paper, 30 cm long and 1 cm broad. The strip was saturated with the salt by moistening with an aqueous solution of it, and drying. The experiments were performed in a tubular Vycor furnace kept at the desired temperature. The strip was supported on a Pyrex bridge between Pyrex boats filled with excess salt. Steel rods were used as electrodes with KCNS, while a steel cathode and platinum anode proved suitable with the nitrate melt. They were inserted through holes in the furnace and dipped into the boats.

*J. Chromatog.*, 11 (1963) 122-123

Results are reported in Table I. The anionic behavior of Zn(II), Co(II), Cr(III), and Re(V) shows that these ions form thiocyanate complexes in molten KCNS solution. In the case of Co(II) and Cr(III), this confirms the spectroscopic evidence of HARRINGTON AND SUNDHEIM<sup>3</sup>. The rhenium (V) thiocyanate complex ( $K_3[ReO_2(SCN)_4]$ )<sup>4</sup> was prepared by reduction of  $KReO_4$  in the presence of KSCN in aqueous

TABLE I

Ion	<i>LiNO<sub>3</sub>-KNO<sub>3</sub> eutectic, 255°</i>		<i>KSCN, 210°</i>	
	Time (h)	Movement (cm) <sup>a</sup>	Time (h)	Movement (cm) <sup>a</sup>
Ag(I)	3	+ 2.5	2	+ 2.5
Tl(I)	1 1/2	+ 5.5	2 1/4	+ 7.5
Co(II)	3	o <sup>b</sup>	3	- 1.5
Cu(II)	3	o <sup>b</sup>	3	+ 2.5 <sup>c</sup>
Zn(II)	2	+ 1.5	3 1/2	- 0.5
Cd(II)	2	ca. + 4	3 1/2	o <sup>b</sup>
Pb(II)	2	+ 4.5	2	+ 1.0
Sn(II)	1 1/2	+ 5.5	2	o
Cr(III)	2	+ 3.0	3 1/2	- 2.0
Bi(III)	1 1/2	+ 4.5	2 1/4	o
Re(V)	—	—	2 1/2	- 2.0

Average voltage gradient for each run *ca.* 10 V/cm).

<sup>a</sup> +: movement towards cathode; —: movement towards anode. Values are from center of initial spot to center of zone after moving.

<sup>b</sup> Insoluble precipitate formed.

<sup>c</sup> May have been converted to Cu (I).

solution, and this orange solution was used as the sample. The anionic motion of the orange zone is evidence that the complex ion is stable under these conditions.

Several other ions which might form thiocyanate complexes, such as Fe(III), and Ni(II), gave an apparently insoluble product, which may have been oxide, in both electrolytes.

We wish to acknowledge the support of one of us (A.S.) by the National Science Foundation under its program of Summer Research Participation for High School Teachers.

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Received September 24th, 1962

*J. Chromatog.*, 11 (1963) 122-123