before a satisfactory treatment for the soil can be worked out.

The results of a recent preliminary investigation into the composition of a tidal mud flat in the Sierra Leone River estuary suggests that a considerable proportion of the sulphur in these soils may possibly be derived from the overlying estuarine water. A series of mud samples from twenty-eight sites, arranged in four equidistant parallel rows, were examined for their organic contents, and in addition the chlorinity and sulphate content of the seepage water was determined. A sample of the estuarine water from the shore of the mud flat was also collected, and its chlorinity and sulphate content determined for comparative purposes.

The single values for chlorinity and sulphate obtained for the estuary water were 16.20 ‰ and 2.148 ‰ respectively. Qualitative determinations for sulphate and chloride carried out on the water from some fresh-water feeder streams within a few weeks of the estuarine determinations showed only a trace of either ion present. This suggests that the bulk of the sulphate in the estuarine water is derived from marine rather than terrestrial sources.

Table 1. AVERAGE CHLORINITY AND SULPHATE CONTENT OF THE SEEPAGE WATER COMPARED WITH THE AVERAGE ORGANIC CONTENT (LOSS ON IGNITION) OF THE MUD COLUMN FOR EACH ROW OF THE SAMPLING PATTERN

Row	No. of samples	Cl (‰)	SO ₄ (‰)	SO ₄ per unit (gm.) Cl	Organic (loss on ignition) (per cent)
1	6	15.1	1.620	0.1073	21.65
2	7	16.7	2.064	0.1236	21.92
3	7	17.1	2.259	0.1321	23.08
4	8	17.1	2.257	0.1320	23.31

In Table 1, the average chlorinity and sulphate content of the seepage water has been compared with the average organic content (loss on ignition) of the mud column for each row of the sampling pattern. Table 1 reads downwards with increased distance from the shore of the mud flat. It will be seen that although the relationship between the organic content and the values for chlorinity and sulphate is not an exact one, it is sufficiently close to indicate that the horizontal gradients in the concentrations of the two constituents are probably due to differential absorption by the organic fraction and also, possibly, by the inorganic colloidal fraction of the mud.

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¹ Rice Research Station, Rokupr. Annual Report for 1957 (Crown Agents for Overseas Govts. and Admins., London, 1958).

Mechanism of the Electroreduction of Complexes of the Type $[M(NH_3)_5X]^{n+}$

THE effect of various anions upon the reduction of $[Co(NH_3)_5X]^{2+}$ at the dropping mercury electrode was reported recently by Vlček and Kůta¹. They explained the generation of the electrochemically active species in terms of a bimolecular substitution process that was proposed earlier² and has since been the subject of correspondence between Dr. Vlček and one of us (G. W. W.).

It was proposed² that cathode current efficiencies observed for the electrodeposition of nickel from

liquid ammonia solutions of spin-free nickel (II) complexes are best interpreted in terms of an S_N2 ligand substitution process and that resultant trans-labilization is probably the rate-determining process. The communication by Vlček and Kůta prompts us to report more recent results in support of this interpretation.

Under conditions strictly analogous to those employed earlier², the cathode current efficiencies found for the electrolysis of liquid ammonia solutions of $[Co(NH_3)_5I](NO_3)_2$, $[Co(NH_3)_5I](NO_3)_2$, and $[Co(NH_3)_5SCN](NO_3)_2$ are 24, 33, and 47 per cent, respectively. Thus, the trend in cathode current efficiency parallels the increasing *trans* effect, as would be predicted on the basis of the work of Watt and Hazlehurst². Moreover, we have found evidence for the *in situ* generation of $[Co(NH_3)_5X]^{2+}$ by electrolyzing $[Co(NH_3)_6]^{3+}$ in the presence of I⁻ and SCN⁻; the observed cathode current efficiencies were 36 and 46 per cent, respectively. Within experimental error, these results are the same as those obtained with *a priori* incorporation of the I⁻ and SCN⁻ ligands.

A more detailed account of these experiments will be published elsewhere.

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¹ Vlček, A. A., and Kůta, J., *Nature*, **185**, 95 (1960).

² Watt, G. W., and Hazlehurst, D. A., *J. Electrochem. Soc.*, **106**, 117 (1959).

A Micro Gas Chromatograph

WE were in need of a gas chromatograph for very small samples, and as a result of a recent paper by Martin¹, we began to construct a katharometer of very small bore. We finally succeeded in stretching a 10 μ tungsten wire 40 mm. long along the axis of a copper tube of 0.4 mm. bore and also of a stainless tube of 0.3 mm. bore, the cell volume of the latter being a little less than 3 μ l. It is possible to construct a detector of still smaller bore. We had only vague ideas as to the column to be used in connexion with this microdetector. The column tube must obviously have a bore comparable with that of the detector. To fill such a capillary with an ordinary support of powder form would be extremely difficult and would require a great deal of effort. We considered, therefore, a support of thin wire or rope form, or better still, the relatively large internal surface of the capillary alone. Then the work of Golay² came to our notice. We tried with success an internally coated empty capillary of 0.3 mm. bore. Two supports of wire or rope form are also very promising, namely, a 0.3-mm. simple copper wire with a few thorn-like protuberances on its surface to keep the wire coaxially inside a 0.5-mm. bore capillary, and a 0.5-mm. double coil of tungsten wire with its central mandrel.

Samples of size ranging from 10⁻⁴ to 10⁻⁵ ml. and sometimes 10⁻⁶ ml. have been injected with a high degree of reliability by means of a hypodermic needle. This holds a capillary ampoule—already opened or still closed—near its nozzle and a rubber stopper in its socket, through which a steel rod can be moved for displacing or crushing the ampoule.