Table 2.

Substance No.	Cu (calc.)	Cu (found)	H (calc.)	H (found)	C (calc.)	C (found)
3	* 21.21	21.25	4.88 ** 5.66	4.44 5.49	30.06 34.32	30.00 34.13
4	23.72	23.37				
5	21.47	21.10				
10	—	—	4.20	3.99	53.62	53.46
12	28.40	28.33	4.5	4.0	32.20	32.50

* Calculated for $(nC_3H_7)_2NCS_2Cu \frac{1}{2} CHCl_3$.

** " " " $(nC_3H_7)_2NCS_2Cu \frac{1}{2} CS_2$.

and some are postulated trimeric. The latter may possibly be built up of copper triangles. Preliminary data from a recently commenced X-ray examination⁴ of one of the postulated trimeric compounds, $(nC_3H_7)_2NCS_2Cu$, seem to support the postulate of its trimericity. It should also be observed here, that several of these trimeric cuprous compounds crystallized with solvents (see Table 1). These solvents could be removed by careful heating *in vacuo* without the crystals being deformed, as far as could be seen. Obviously, these trimeric compounds are so packed that a crystal structure with "hollow spaces" could be well imagined. These "hollow spaces" can thus, partly or entirely, be filled out by the organic carbon chains, provided that these chains are large enough (*e. g.* $(nC_4H_9)_2NCS_2Cu$). They can also be filled by solvents (*e. g.* $(nC_3H_7)_2NCS_2Cu \cdot 1/2 CHCl_3$).

It is remarkable that a change from a tetrameric to a trimeric structure takes place in the series of cuprous *n*-dialkyl-dithiocarbamates if the carbon chain is increased by one carbon atom. It should be observed that the only trimeric copper compounds which, up to this time, have been published, are some esters of phosphoric acid⁵ (*e. g.* $CuClP(OPr-iso)_3$). The cuprous di-*isopropyl*-dithiocarbamate may possibly be high polymeric.

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Determination of Small Amounts of Deuterium Oxide in Water by Infra-red Spectroscopy

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In studies of isotope effects it was of interest to know the absolute deuterium concentration of various deuterium substituted organic compounds. For that reason the compounds were burned to water and the deuterium content of the water was determined by means of infra-red spectroscopy. A method, similar to that of Thornton and Condon¹, but more accurate, has been worked out.

Experimental. The measurements were carried out on a Perkin-Elmer infra-red spectrometer, model 112, with a NaCl-prism. The cell thickness was about 0.05 mm and its windows were made of CaF₂. The slit width used was 0.050 mm. A number of standard samples were made from deuterium water containing 99.84 % D₂O, $d_2^0 = 1.10521$ (Norsk Hydro), and ordinary distilled water. Care was taken to prevent undue dilution by exchange with atmospheric moisture.

At each determination, the whole absorption band at 3.98 μ (2 513 cm⁻¹) was recorded to eliminate a possible error in the wavelength setting, but the reading was always taken at exactly 3.98 μ . The absorption of ordinary distilled water in the same cell was always checked between the analyses. After each recording the cell was washed with acetone and dried by blowing dry nitrogen through it. No memory effect was found in the cell even when the D₂O concentration exceeded 5 % D₂O.

A calibration curve was drawn and a straight line was obtained by the method of least squares. As there will always be an error both in the determination of the absorption of ordinary water, I_0 , and in that of the sample, I , the line need not pass the origin but has a small intercept on the ordinate. The equation of the line was found to be:

$$\log \frac{I_0}{I} = 0.3174c - 0.0034$$

where c is the concentration measured in per cent by weight. In Table 1 we see

Table 1. Weighed out quantities of D₂O (wt %) in ordinary water, c_{true} , compared with the values obtained from the equation, c_{found} . $\Delta = c_{\text{true}} - c_{\text{found}}$.

c_{true}	c_{found}	$\Delta 10^{-3}$
0.0163	0.0107	+5.6
0.3053	0.3091	-3.8
0.5466	0.5436	+3.0
0.8707	0.8804	-9.7
1.1161	1.1130	+3.1
1.3515	1.3547	-3.2
1.6497	1.6442	+5.5

the true concentrations compared with those calculated from the equation. $\Delta = c_{\text{true}} - c_{\text{found}}$; e = mean error in a

single determination = $\sqrt{\frac{\sum \Delta^2}{n-2}} = 6 \times 10^{-3}$ wt %.

Corrections were made for the natural occurrence of heavy water in distilled water assuming² its concentration to be 0.0163 wt %.

In the present investigation, Beer's law is obeyed and a straight line is obtained when plotting optical density against concentration. In a work of Gaunt³, Beer's law was not obeyed since he used a too large slit width. This also caused some overlapping from the absorption band of the carbon dioxide at 4.25 μ (2 353 cm⁻¹). Under these conditions the accuracy of Gaunt's experiments cannot be as high as 1 % as he claimed, even if he included only concentrations up to 0.8 % D₂O. With the method of least squares (straight line), the mean error in his experiments is found to be 2 %. The assumption of a straight line was made as all the points up to concentrations of about 0.6 % fall on a straight line, but at concentrations higher than this the curvature begins, and after 0.8 % it will be appreciable.

In the present work the absorption band of HOD at 3.98 μ was well separated from other absorption bands and no overlapping could be observed. The absolute mean error in a single determination is found to be ± 0.006 wt % for concentrations up to 1.3 % D₂O.

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