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Studies on the Neutral Sulfur of Urine. Criticism of the Iodimetric Titration of Diethylsulfide.*

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Abel[1] found diethylsulfide in dogs' urine which had been treated with calcium hydroxide. Christomanos[2] determined the amount of the sulfide in urine by iodimetry, basing his method upon the formation of the addition product of diethylsulfide and iodine, $(C_2H_5)_2SI_2$, previously reported by Cahours.[3]

TABLE I.

Iodine taken up by Et_2S from I_2 solutions, with variation in the different components of the system.

Conc. KI mols per l. × 10^2	Conc. I_2 mols per l. × 10^2	Conc. HI mols per l. × 10^2	Conc. H ions* mols per l. × 10^2	Et_2S Mols × 10^3 added to 1 l. sol.	I_2 Mols × 10^3 taken up	Ratio $\frac{I_2}{Et_2S}$
2.4	1.0			1.46	3.09	2.16
6.0	1.0			0.96	1.22	1.27
18.0	1.0			1.34	0.25	0.86
24.0	1.0			1.27	0.21	0.17
6.0	0.265			1.32	0.15	0.11
6.0	0.505			1.00	0.35	0.35
6.0	0.790			0.92	0.72	0.70
6.0	1.00			0.96	1.32	1.27
6.0	2.61			1.23	3.13	2.56
6.0	2.0			6.66	10.55	1.59
6.0	2.0			16.48	17.48	1.06
6.0	2.0			20.52	18.28	0.89
6.0	2.0			24.22	18.89	0.78
6.0	2.0			35.58	19.45	0.55
	2.0	8.0		1.83	2.80	1.53
	2.0	8.0		6.55	9.47	1.46
	2.0	8.0		17.95	16.77	0.93
	2.0	8.0		24.30	18.42	0.76
	2.0	8.0		34.61	19.00	0.55
	2.0		8.0	1.85	2.80	1.53
	2.0		6.0	1.81	2.76	1.52
	2.0		5.0	2.03	2.95	1.45
	2.0		3.0	2.27	3.22	1.42
	2.0		1.0	2.00	2.75	1.38
	2.0		0.0	1.80	2.29	1.27

*Hydrogen ion concentration was calculated by assuming the hydrogen iodide to be totally ionized. 0.04*N* iodine solutions in 0.08*M* KI and 0.08*M* HI were combined in various ratios so that the total concentration of electrolyte might remain constant.

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1 Abel, J. J., *Z. physiol. Chem.*, 1896, **20**, 253.

2 Christomanos, A. A., *Z. physiol. Chem.*, 1933, **217**, 177.

3 Cahours, *Ann. d. chim. et d. phys.*, 1865, **135**, 355.

The authors have been unable to confirm this stoichiometric relationship under the conditions described by Christomanos and investigated the factors influencing the distribution of iodine in the system, diethylsulfide—aqueous solutions of potassium iodide.

The experiments were carried out as follows: The diethylsulfide was weighed by difference from a weighing burette into 500 cc. volumetric flasks embedded in an ice-water mixture ($t = 2°$ to $5°$) and containing iodine, potassium iodide and hydrogen iodide. The mixtures were shaken until equilibrium was reached with respect to the iodine distribution. A portion of the mixture was centrifuged at 2° to 5°, and 25 cc. of the clear aqueous solution were subjected to iodimetric titration. The results are shown in Table I.

Results. The amount of iodine taken up by diethylsulfide varies with the amount of the sulfide and also with the concentration of iodine, iodide ion and hydrogen ion, the effect of the last factor being the slightest. This suggests that the removal of iodine from its solution by diethylsulfide is due to the solubility of iodine in the sulfide. In fact, iodine was found to be miscible with diethylsulfide roughly in all proportions.

In the light of the present experimental results the method for the determination of diethylsulfide in biological solutions should, therefore, be based upon other principles.

Summary. The amount of iodine taken up at a constant temperature by diethylsulfide is the function of the concentrations of iodine, iodide ion and hydrogen ion in addition to the amount of diethylsulfide added, and there is no such chemical relation under the experimental conditions as expressed by the equation:

$$(C_2H_5)_2S + I_2 = (C_2H_5)_2SI_2$$

The analytical method based upon this erroneous principle is unreliable.

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Effects of Avian Pituitary Glands in Salamanders.

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Induction of ovulation has been secured in various forms by administration of implants or extracts of the pituitary glands of