MODIFICATION OF THE DUMAS TECHNIQUE FOR SUBSTANCES DIFFICULT TO BURN

Sir:

When a large number of nitrogen determinations by the Dumas method is to be made it is common practice to abandon the classical method, which requires emptying and refilling the combustion tube for each determination, and instead to proceed as in the determination of carbon and hydrogen, weighing the substance into a combustion boat, covering it with fine copper oxide and inserting it into the posterior end of the filled tube. This method has obvious advantages that do not need comment here. However, in the case of substances that are difficult to burn this modification may lead to low results because of incomplete combustion. In the work on the lupine alkaloids being conducted in this Laboratory it was found that some of these substances could not be analyzed in this way on account of the fact that they yielded non-volatile split products that were deposited on the walls of the tube out of contact with copper oxide and were not thoroughly oxidized.

A method for overcoming this difficulty while preserving the advantages of the general method has been developed and is here described for the benefit of those who may encounter similar difficulties. In principle the new technique involves mixing the weighed substance with a large excess of copper oxide and packing this into a metal tube which is then inserted into the combustion tube in the location ordinarily used for the combustion boat. We are using a copper tube 15 cm. long and 1.27 cm. external and 1 cm. internal diameter. The tube is ignited, cooled and filled as follows.

The forward end of this tube, which we refer to as a cartridge, is loosely plugged with a centimeter long roll of copper gauze. Upon this is poured with the aid of a solid funnel about two centimeters of previously ignited fine copper oxide,[1] then the substance mixed with copper oxide enough to form a layer of ten to twelve centimeters is poured in, the mortar is rinsed with fine copper oxide and the rinsing added to the cartridge until it is filled. It may now be inserted in the combustion tube, backed in the usual manner with a roll of oxidized copper gauze and the combustion carried out according to the classical technique.

At the conclusion of the analysis the cold cartridge may be emptied of its spent charge and if it is handled with tongs will be ready for a new charge without reignition.

Somewhat high results may be expected from the use of such a cartridge because the air adsorbed on the fine copper oxide cannot be displaced completely by the carbon dioxide stream. Blank runs, however, indicate that the error due to this factor is no greater than that encountered in the ordinary technique. The excess air due to the cartridge amounts, on the

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(1) Copper oxide is usually sufficient, but the cartridge may be filled with lead chromate or with mixtures of catalytic oxides when desirable.

average, to 0.2 cc. The results obtained by this method have been satisfactory as the following table will indicate.

Substance	% N without cartridge	% N with cartridge	Calcd.
Sparteine mercuric chloride	2.01	4.83	4.86
Alkaloid A from *Lupinus caudatus*	5.90 6.17 9.62 9.73	10.03 10.13	10.02
Alkaloid from *Lupinus cruckshanksii*	6.97 9.60	10.34 10.23	
Alkaloid from *Lupinus palmeri*	9.54 9.31	9.97 10.07	
Alkaloid from *Lupinus andersoni*	6.61 6.51	10.47	

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RECEIVED DECEMBER 23, 1932 PUBLISHED FEBRUARY 9, 1933

CONCERNING THE EXISTENCE OF THE SO-CALLED HEATS OF TRANSFER (Q^* VALUES) IN PELTIER HEATS

Sir:

To explain the Ludwig-Soret effect, Eastman [THIS JOURNAL, **48,** 1482 (1926)] introduced the concept of the heat of transfer (Q^*) [the heat of transfer of a mole of component A is designated as $\overline{Q}_A$ by Eastman], a latent heat which appears at some point in a homogeneous solution when a mole of dissolved component is transferred from this point to another place in the solution. The same quantity occurs in a discussion of electrolytic thermal forces. Wagner [*Ann. Physik,* (5) **3,** 629 (1929)] and later Lange and co-workers [Lange and Mischtschenko, *Z. physik. Chem.,* **A149,** 1 (1930)] extended these considerations to the electrolytic Peltier heats. According to them

$$ {}_{\text{metal/solution}}\pi_i = T({}_{\text{metal}}\bar{S}_i - {}_{\text{solution}}\bar{S}_i) - z_iQ^*_\theta - n_CQ^*_C + n_AQ^*_A \qquad (1) $$

(π_i is the Peltier heat given up at the anode by a mole of the potential determining ion i of valence z_i, n_C and n_A are transference numbers and Q^*_C and Q^*_A are molar heats of transfer of cation and anion).

To date the following evidence for the existence of these novel heat effects (Q^*) could be advanced: (1) Eastman [THIS JOURNAL, **50,** 292 (1928)] found a certain agreement between the Q^* values determined from Ludwig-Soret coefficients and estimated from suitable thermo-electric measurements.

(2) Thermo-electric forces between differently oriented single crystals of the same metal can only be explained by Q^* values depending on direction [Wagner, *loc. cit.*] if one does not wish to postulate a directional dependence of $\bar{S}$.

(3) Measurements of the Ludwig-Soret effect and of thermoelectric forces on solid salts and mixed crystals have been explained by use of heats of transfer [Reinhold, *Z. physik. Chem.,* **B11,** 321 (1931)].

All these proofs rest on measurements made on non-isothermal systems,