Surface and Micellar Properties of a Long-Chain Nonionic Surfactant

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Abstract □ In order to study the surface-chemical behavior of a highly polyoxyethylated surfactant without the masking influence of species of low degrees of polyoxyethylation, a dodecanol adduct with an average of 30 ethylene oxide molecules, $C_{12}(EO)_{30}$, was stripped of low molecular weight species, up to $C_{12}(EO)_6$ or $C_{12}(EO)_{10}$, by molecular distillation. The components of highest molecular weight and polyethylene glycols were removed by ultrafiltration, leaving a product of rather narrow molecular weight distribution with the average composition $C_{12}(EO)_{28}$. Surface tension-concentration relationships, measured at 15, 25, 40, and 55°, were used to derive values for the following parameters: critical micelle concentration (CMC), plateau surface tension above the CMC, surface excess and limiting area per surfactant molecule adsorbed at the water/air interface, and free energy, enthalpy, and entropy changes of micellization. Reduced hydration of the polyoxyethylene portion of the surfactant with increasing temperature lowered its hydrophilic-lipophilic balance. This resulted in lower CMC and plateau surface tension values, smaller area per molecule at the water/air interface, and greater negative free energy of micelle formation. The heat and entropy change of micelle formation were constant and positive between 15 and 55°. This indicates that the latter is responsible for the formation of micelles. The corresponding increase in randomness was attributed mainly to water surrounding the hydrocarbon chains of single surfactant molecules and trapped in their coiled polyoxyethylene chains, which loses its contact with the surfactant molecules and hence its structure when they aggregate into micelles. These properties were compared with those of a surfactant of nearly the same average degree of polyoxyethylation but containing a fraction of low degree of polyoxyethylation.

Keyphrases □ Surfactants, long-chain, nonionic—surface, micellar properties □ Surface tension-concentration relationship—surfactants □ Entropy, enthalpy, free energy—micelle formation □ CMC, plateau surface tension above CMC—surfactants □ Area limit, surface excess—surfactant molecules

The thermodynamics of micelle formation is conveniently studied by measuring the temperature dependence of the critical micelle concentration (CMC). In the case of nonionic surfactants prepared by the addition of ethylene oxide (EO) to alcohols and phenols, there arises a complication owing to the fact that this reaction is a random process resulting in products which have a range of polyoxyethylene (POE) chain lengths and of molecular weights. The latter parameter fits approximately a Poisson distribution. Micelle formation of such surfactants is very strongly influenced by the shortest-chain species because these are the most surface-active ones (1), and are sometimes even insoluble in water. The CMC and its temperature dependence are not so much characteristic of the nominal or average degree of polyoxyethylation but depend largely on the amount of the least polyoxyethylated species.

This difficulty has been circumvented by working with homogeneous surfactants prepared by synthetic methods rather than by the addition of EO (2–6). Because such methods become increasingly laborious as the number of EO units increases, they have been applied only to surfactants of very short POE chains. Another approach has been to narrow the molecular weight distribution of EO addition products by molecular distillation (7). However, this process too is only feasible for surfactants of relatively low molecular weight; surfactants of high degrees of polyoxyethylation undergo extensive decomposition while being molecularly distilled owing to the high temperatures required (see below). For instance, an EO adduct of *n*-dodecanol containing an average of 30 EO units, $C_{12}(EO)_{30}$, which had been molecularly distilled, was found to contain appreciable amounts (9 ± 4 wt. %) of material with composition $C_{12}(EO)_n$ where $n \leq 6$ by TLC (8), and some polyethylene glycol by ultrafiltration (9). Dodecanol-based surfactants of $n \leq 5$ have cloud points below 15°, *i.e.*, they are practically insoluble in water over the entire temperature range studied, and are solubilized by the surfactant fractions of longer POE chains. Thus, the CMC data published for this highly polyoxyethylated surfactant (7, 9, 10) are not representative of its high average degree of polyoxyethylation because the product contains a low molecular weight fraction, which affects the CMC and thereby the thermodynamic parameters of micelle formation to a greater extent than the amount in which it is present (see *References* 1, 6). The purpose of this work was to study the micellization of a highly polyoxyethylated nonionic surfactant freed of the fractions of low degrees of polyoxyethylation.

EXPERIMENTAL

The present approach was to start with a Poisson-distribution surfactant prepared by adding an average of 30 EO units to *n*-dodecanol, and to strip off unreacted dodecanol and the species of lowest molecular weight, up to about $C_{12}(EO)_6$, in a molecular still.[1] By distilling only the most volatile components, the still temperature could be kept low enough to prevent significant degradation of the residual surfactant, which constitutes the main fraction. Polyethylene glycols and the most highly polyoxyethylated surfactant fraction were separated by ultrafiltration (9). Additional material of low degree of polyoxyethylation was removed by foam fractionation of the surfactant in a more dilute solution, working with nitrogen at a high reflux ratio. The remaining solution was freeze-dried. The resultant surfactant exhibited no minimum in the surface tension-log concentration plots. The sharp break in these plots is an indication that the molecular weight distribution of the surfactant was fairly narrow.

The absence of components with six or fewer EO groups was verified by TLC (8). The average composition was found to be $C_{12}(EO)_{28}$ by a procedure based on its IR spectrum (9), which was free of carbonyl.

This average composition is close to that of the $C_{12}(EO)_{30}$ compound of broader molecular weight distribution, for which the micellar (7, 9) and surface properties (10) have been reported. This will permit one to evaluate the effect of molecular weight distribution, in particular the presence of low molecular weight components, on these properties.

For a small amount of the surfactant, the stripping by molecular distillation was carried somewhat further despite progressive decomposition, removing species up to about $C_{12}(EO)_{10}$. Purification

[1] Courtesy of General Aniline and Film Corp.

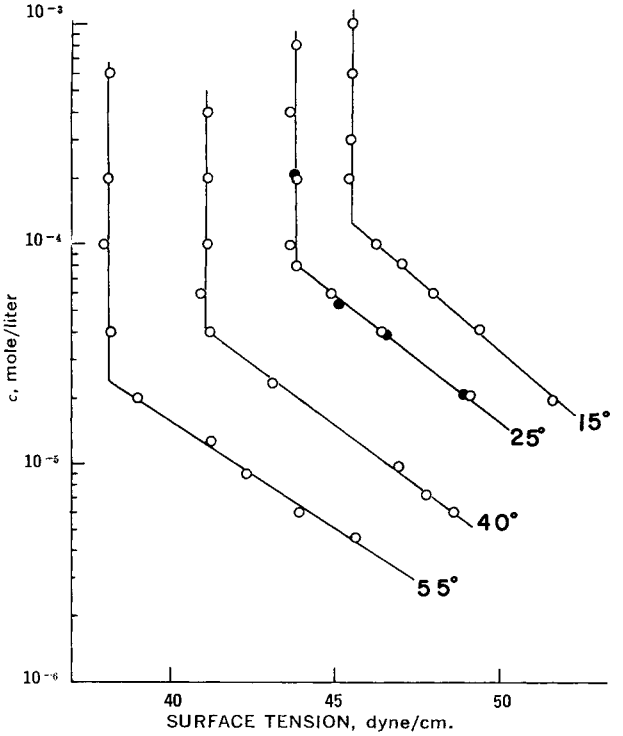

Figure 1—*Surface tension-log concentration plots of $C_{12}(EO)_{28}$ at various temperatures. Solid circles refer to a more extensively stripped sample.*

by ultrafiltration and by foam fractionation was followed by a treatment with decolorizing carbon. With regard to the properties tested, namely, composition and surface tension-concentration relationships at 25°, the second batch was practically indistinguishable from the main lot. This provides another indication that the purified surfactant had a fairly narrow molecular weight distribution.

Distilled water redistilled from alkaline permanganate was used throughout. Surface tensions were measured with a Wilhelmy balance provided with sand-blasted platinum blade. The surfactant solutions were contained in 250-ml. short-neck boiling flasks with 40/50 standard taper joints. These wide openings permitted insertion of the Wilhelmy plate. All solutions were stored overnight in a constant-temperature bath controlled to within ±0.05° prior to measuring surface tensions.

TREATMENT OF DATA

The surface tension-log concentration plots at four temperatures are shown on Fig. 1. Concentrations c are expressed as mole/liter. Each plot consists of two straight lines which intersect at the CMC. Above the CMC, the plots are horizontal within the precision of the measurements; the values of these constant surface tensions are listed in Table I in the column headed "plateau γ."

The values of the slopes of the plots below the CMC are also listed in Table I, as well as those of the surface excess Γ (mole/cm.²). The latter were calculated by means of the Gibbs adsorption isotherm

$$\Gamma = -\frac{1}{2.303RT}\frac{d\gamma}{d\log c} \qquad \text{(Eq. 1)}$$

The assumption inherent in Eq. 1, that the activity coefficient of the dissolved surfactant is unity, is probably justified by the low concentrations.

The area per surfactant molecule adsorbed at the water-air interface (A, in Å² units) was calculated by

$$A = 10^{16}/\Gamma N \qquad \text{(Eq. 2)}$$

where N is Avogadro's number. These values refer to bulk concentrations just below or at the CMC.

It is convenient to consider micelle formation (subscript m) as the change from a hypothetical initial standard state (superscript o) represented by the hydrated monomer at unit mole fraction, to the hydrated micelle at unit mole fraction. The activity coefficient of the single molecules is unity, *i.e.*, they behave as if they were at infinite dilution (3, 11). This differs from the phase-separation model (6, 7, 12), in which a mole of single surfactant molecules at the CMC forms micelles, and for which $\Delta\bar{G}_m = 0$ and hence

$$\Delta\bar{S}_m = \Delta\bar{H}_m/T \qquad \text{(Eq. 3)}$$

Treating micelle formation as a phase change has the advantage of simplicity but is difficult to reconcile with Gibbs' phase rule (14). The result (3) is

$$\Delta G_m^\circ = 2.303RT \log C \qquad \text{(Eq. 4)}$$

where C is the CMC expressed as mole fraction, *i.e.*, $C \cong$ CMC/55.34.

The mass-action model (14) results in an equation which reduces to Eq. 4 for large micelles (3, 13). This condition is fulfilled by $C_{12}(EO)_{28}$, which has an aggregation number of 58 (15).

Combining

$$\Delta G_m^\circ = \Delta H_m^\circ - T\Delta S_m^\circ \qquad \text{(Eq. 5)}$$

with Eq. 4 gives

$$\log C = \frac{\Delta H_m^\circ}{2.303RT} - \frac{\Delta S_m^\circ}{2.303R} \qquad \text{(Eq. 6)}$$

If ΔH_m° and ΔS_m° are independent of temperature, a plot of log C *versus* the reciprocal of the absolute temperature is a straight line with the slope equal to $\Delta H_m^\circ/2.303R$ and the intercept (at $1/T = 0$) of $-\Delta S_m^\circ/2.303R$. A condition implicit in this treatment is that the size of the micelles remain constant and independent of temperature (3, 14).

RESULTS AND DISCUSSION

Surface Properties—As is seen from Table I, the plateau surface tension decreases with increasing temperature, because the surface excess increases. This is a consequence of the lower hydration of the EO groups at the higher temperatures, which reduces the hydrophilic-lipophilic balance and thereby renders the surfactant molecules more surface-active. The plateau surface tensions of $C_{12}(EO)_{30}$ having a broader molecular weight distribution were 0–3 dynes/cm. lower at comparable temperatures (7, 10), owing to the presence of the low molecular weight fraction. Similar differences have been observed with polyoxyethylated octylphenols (1). The increase in surface excess with increasing temperature results in smaller limiting areas per surfactant molecule adsorbed at the water-air interface. The magnitude of the variation of these three parameters in Table I between 15 and 55° is about the same, namely, 15% of the value at 15°. This is a larger variation than is commonly observed with polyoxyethylated surfactants (3, 5), because the surfactant used here has a longer POE chain.

As expected, the area per surfactant molecule at the water-air interface of the $C_{12}(EO)_{30}$ surfactant of broader molecular weight distribution is nearly the same as that of the more highly fractionated $C_{12}(EO)_{28}$ (10). However, the latter value decreased more than three times as much with increasing temperature as the former.

It is of interest to compare the limiting area per $C_{12}(EO)_{28}$ molecule at the water-air interface with the cross-sectional area of a randomly coiled POE chain of 28 units in water. The underlying assumptions are that the POE moiety of the surfactant molecules in the adsorbed monolayer is randomly coiled and approximately spherical, and that the packing density of the monolayer is limited by the cross-section of those coils.

The radius of gyration of a POE chain is estimated by a random walk calculation, using the restriction of tetrahedral bond angles (16), as

$$R = 2LP^{1/2}/6^{1/2} = 11.2 \text{ Å} \qquad \text{(Eq. 7)}$$

The average bond length

$$L = \frac{(2)(1.54) + 1.43}{3} = 1.50 \text{ Å}$$

Table I—Solution Properties of $C_{12}(EO)_{28}$

Temperature, °C.	CMC, mole/liter × 10^4	Plateau γ, dyne/cm.	$-(d\gamma)/(d \log c)$, dyne/cm.	Γ, mole/cm.^{2} × 10^{10}	Area per Molecule, Å^2	$\Delta G°$, kcal./mole
15	1.24	45.5	7.74	1.404	118	−7.45
25	0.79	43.8	8.66	1.518	109	−7.97
40	0.42	41.1	9.57	1.597	104	−8.77
55	0.24	38.1	10.22	1.627	102	−9.55

and the number of bonds $P = 28 \times 3 - 1 = 83$. The cross-sectional area $\pi R^2 = 391$ Å^2. Even though this is a low estimate, it is considerably greater than the measured limiting area per $C_{12}(EO)_{28}$ molecule at the water-air interface, indicating considerable distortion or interpenetration of the POE moieties of the surfactant molecules (10, 17).

Thermodynamic Properties—As can be seen on Fig. 2, the plot of log *C versus* $1/T$ is a straight line, described by

$$\log C = -11.55 + 1700/T \qquad \text{(Eq. 8)}$$

From the slope, $\Delta H_m° = (1700)(2.303)(1.987) = 7780$ cal./mole = 7.78 kcal./mole. For $1/T = 0$, $\Delta S_m° = (2.303)(1.987)(11.55) = 52.85$ cal./degree mole.

Micelle formation of nonionic surfactants is usually an endothermic process (3–7, 11–13, 19). The heat of micelle formation of the $C_{12}(EO)_{30}$ surfactant of broader molecular-weight distribution was 3.5 kcal./mole (7), *i.e.*, less than one-half of the value found for the more highly fractionated $C_{12}(EO)_{28}$. At least part of the difference in $\Delta H_m°$ can be attributed to the solubilization of the lowest molecular-weight, water-insoluble fraction of the former by micelles.

The entropy and free energy changes of $C_{12}(EO)_{30}$ had to be recalculated according to Eqs. 4–6, because in the original publication (7) the former was calculated according to Eq. 3 and the latter was assumed to be zero. The $\Delta S_m°$ value obtained for $C_{12}(EO)_{30}$, 36 cal./degree mole, is only two-thirds of that of $C_{12}(EO)_{28}$. The differences in $\Delta G_m°$ of the two surfactants at corresponding temperatures are smaller, because the surfactant with the larger $\Delta S_m°$ value had also the larger $\Delta H_m°$ value.

Linearity of log *C versus* $1/T$ plots is not always observed. For $C_{10}(EO)_4$ and $C_{10}(EO)_5$, they were curved; for $C_{10}(EO)_8$, the points for all but the highest temperature (34°) fell on a straight line (5). The lack of linearity may be a consequence of an increase in the micellar molecular weight (MMW) with increasing temperature (3), which has been observed for surfactants of low degrees of polyoxyethylation (18). For somewhat more highly polyoxyethylated surfactants, only small increases in MMW with temperature were observed until a threshold temperature, about 25° below the cloud point, was reached (19). Possibly, the threshold temperature of $C_{10}(EO)_8$ was exceeded at 34°, hence its MMW at that temperature was markedly greater than at the lower temperatures, and for this reason the 34° point fell below the straight line of the log *C versus* $1/T$ plot.

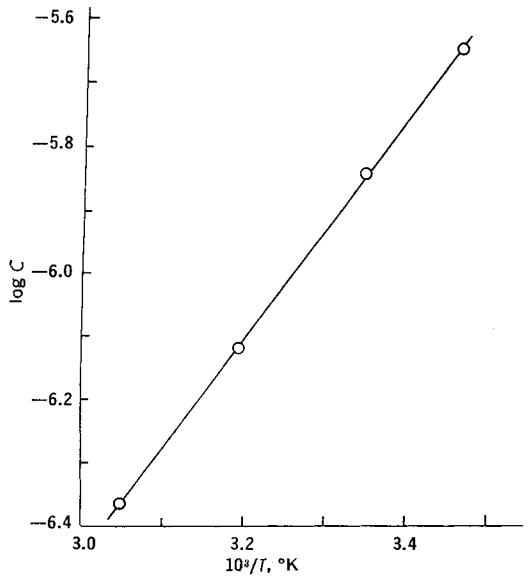

Figure 2—*Plot of the logarithm of the CMC (expressed as mole fraction)* versus *the reciprocal of the absolute temperature.*

Considering that the heat of micellization is positive, it is the positive entropy change which is responsible for the negative free energy change and for the formation of micelles. Positive entropy change indicates increased randomness. Most likely, this means diminished water structure. The currently held view (4, 12, 14) is that water surrounds the hydrocarbon chain of a single surfactant molecule like a cage and has an "iceberg" structure. Transfer of this hydrocarbon chain from the aqueous environment into the interior of a micelle destroys this structure. The hydrocarbon chain may also gain some conformational entropy in the process.

However, this does not account for all of the 53 e.u., because homogeneous surfactants based on decanol and hexadecanol of low degrees of polyoxyethylation have $\Delta S_m°$ values of only 20 to 30 e.u. (4, 5, 14). The difference is probably due to the gain in entropy of the water trapped in the coiled POE chains of the single surfactant molecules, which is squeezed out when micellization occurs. The maximum hydration of an ether linkage is 2 water molecules (20), but long POE molecules trap additional water in between their randomly coiled chains. When $C_{12}(EO)_{28}$ molecules aggregate into micelles, the POE chains surrounding the spherical core formed by the hydrocarbon portion of the molecules become very crowded owing to the relatively small volume available compared to the length of the chains. Most of the water previously trapped in the POE chains is released: $C_{12}(EO)_{28}$ micelles hold an average of only 2.35 water molecules per EO group. When the micellar hydrocarbon core offers a larger surface and the POE chains are shorter, they are less densely packed and can trap large amounts of water. Micelles of $C_{16}(EO)_{21}$ hold 6 water molecules per EO group (21). Since water trapped in the coiled POE chains is more highly ordered than free water, the release of water during micelle formation of $C_{12}(EO)_{28}$ results in an entropy increase. Within this framework, the lower $\Delta S_m°$ value for $C_{12}(EO)_{30}$ could be due to the fraction of low POE content, which relieves the crowding of the POE chains in the micelle somewhat and thereby results in higher hydration.

The decrease in CMC and in standard free energy of micellization with increasing temperature are consequences of the decrease in hydration of the POE part of the surfactant with increasing temperature. In view of the importance of entropic factors, reduction in water structure due to rising temperature may well be a contributory cause.

REFERENCES

(1) E. H. Crook, D. B. Fordyce, and G. F. Trebbi, *J. Phys. Chem.*, **67**, 1987(1963).

(2) H. Lange, *Proc. Intern. Congr. Surface Activity, 3rd Cologne*, **1**, 279(1960).

(3) J. M. Corkill, J. F. Goodman, and S. P. Harrold, *Trans. Faraday Soc.*, **60**, 202(1964).

(4) J. M. Corkill, J. F. Goodman, and J. R. Tate, *ibid.*, **60**, 996(1964).

(5) R. A. Hudson and B. A. Pethica, *Proc. Intern. Congr. Surface Activity 4th Brussels*, **2**, 631(1964).

(6) E. H. Crook, G. F. Trebbi, and D. B. Fordyce, *J. Phys. Chem.*, **68**, 3592(1964).

(7) M. J. Schick, *ibid.*, **67**, 1796(1963).

(8) K. Buerger, *Z. Anal. Chem.*, **196**, 259(1963).

(9) H. Schott, *J. Phys. Chem.*, **68**, 3612(1964).

(10) M. J. Schick, *J. Colloid Sci.*, **17**, 801(1962).
(11) K. W. Herrmann, *J. Phys. Chem.*, **66**, 295(1962).
(12) P. H. Elworthy and A. T. Florence, *Kolloid-Z.*, **195**, 23 (1964).
(13) L. Benjamin, *J. Phys. Chem.*, **68**, 3575(1964).
(14) D. G. Hall and B. A. Pethica, in "Nonionic Surfactants," M. J Schick, Ed., Marcel Dekker, New York, N. Y., 1967.
(15) H. Schott, *J. Phys. Chem.*, **70**, 2966(1966).
(16) C. Tanford, "Physical Chemistry of Macromolecules," Wiley, New York, N. Y., 1963, pp. 150, 156.
(17) M. J. Schick, S. M. Atlas, and F. R. Eirich, *J. Phys. Chem.*, **66**, 1326(1962).
(18) R. R. Balmbra, J. S. Clunie, J. M. Corkill, and J. F. Goodman, *Trans. Faraday Soc.*, **60**, 979(1964).
(19) P. H. Elworthy and C. McDonald, *Kolloid-Z.*, **195**, 16 (1964).
(20) H. Schott, *J. Chem. Eng. Data*, **11**, 417(1966).
(21) H. Schott, *J. Colloid Interface Sci.*, **24**, 193(1967).

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Determination of Trace Amounts of Selenium in Pharmaceuticals

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Abstract □ A quantitative method for the determination of less than 30 p.p.m. selenium in organic sulfur-containing drugs has been developed. The procedure utilizes oxygen flask combustion for decomposition of the organic matter and colorimetric measurement of selenium after reacting with 2,3-diaminonaphthalene, a specific complexing agent for selenium. At the level of 30 p.p.m., better than 90% recovery is obtained. The method is rapid, specific, and free from interferences.

Keyphrases □ Selenium determination—trace amounts □ Oxygen flask combustion, organic material—selenium determination □ Colorimetric analysis—spectrophotometer □ 2,3-Diaminonaphthalene—color reagent

The heavy demand for sulfur has resulted in a downgrading of the quality of the sulfur used with the result that some sulfur can contain up to 0.5% selenium. Consequently, drugs which contain sulfur, or where sulfur-containing compounds are used in the manufacture, may be contaminated with selenium. In addition some drugs require selenium or its compounds in the manufacturing process. Selenium is a toxic element with the same order of toxicity as arsenic, however some investigators (1, 2) suggest that it is essential for some animals under defined conditions. The necessity of controlling the quantity of selenium in drugs is evident.

Many methods are reported in the literature for the determination of selenium in organic and biological materials (2). For compendial purposes it was necessary to select a procedure that would have a wide range of applicability and which would not require unusual equipment. X-ray fluorescence (3) was considered to be out of the realm of most laboratories at the present, as is atomic absorption (4–6). It was therefore necessary to select the best procedures for digestion of the sample and colorimetric measurement, and then to apply the selected procedure to the determination of selenium in those compounds which will be official in USP XVIII and NF XIII which might be contaminated with selenium.

PROCEDURES

Digestion—Wet ashing techniques have been widely used for destruction of the organic material prior to trace element determination. A study of wet digestion procedures prior to selenium analysis was carried out by Gorsuch (7) using isotope tracers to determine selenium recovery. The oxidation mixtures examined were (*a*) nitric and perchloric acids; (*b*) nitric, perchloric, and sulfuric acids; and (*c*) nitric and sulfuric acids. Wet digestion using nitric and perchloric acids was found to be most suitable to prevent losses of the element. Difficulties in the recovery of selenium after the destruction of organic material by wet ashing have been reported; Fogg and Wilkinson (8) reported losses using nitric and sulfuric acids but were able to obtain complete recovery using perchloric acid. Klein (9) recommended a partial oxidation with mercuric oxide present to "fix" the selenium. Grant (10), Cousins (11), and Watkinson (12) have all reported the successful use of nitric-perchloric acid mixtures for digestions of various biological tissues. A mixture of nitric and perchloric acids, and hydrogen peroxide is used by the Food Chemicals Codex (FCC) (13) for the digestion of several organic and inorganic chemicals. However, in all work reported with acid hydrolysis of the sample, losses are prevented only if the conditions of the digestion are carefully controlled and the sample is heated slowly without charring until all selenium has been converted to selenite. The recovery of selenium is low if the perchloric acid is concentrated to the stage when it becomes yellow through autodecomposition, which at this point is accelerated by even 0.5 mcg. of selenium. This is complicated by the fact that the yellow color of incompletely oxidized samples after removal of nitric acid can be confused with the yellow decomposition products of the acid.

The difficultly oxidizable nature of the organic sulfur-containing drugs precludes the use of wet digestion techniques as the organic material cannot be completely removed until the temperature of digestion is raised to a point where excessive losses of selenium occur.

PROCEDURES

Combustion—Combustion in a closed system to eliminate volatilization losses of selenium was first reported by Gutenmann and Lisk (14) who determined selenium in oats using oxygen flask combustion for destruction of the organic material. The oxygen flask technique has since been studied and/or improved by other workers. Dye *et al.* (15) studied oxygen flask combustion for a variety of plant and animal tissues, determining the selenium recovery by radiotracer techniques and using water, HCl, and NaOH as absorbing media. Allaway and Cary (16), Watkinson (17), Cukor *et al.* (18), and Tausky *et al.* (19) have reported successfully on the use of the oxygen flask technique.