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I thought the attached abstracts might be of interest to you. 9/3/71

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AMERICAN CHEMICAL SOCIETY DIVISION OF

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J. C. White, Chairman

R. S. Juvet, Jr., Secretary

MONDAY MORNING - SECTION A - SYMPOSIUM ON CRITICAL ANALYTICAL PROBLEMS FACING GOVERNMENT LABORATORIES - W. W. Meinke, Presiding

1. CRITICAL ANALYTICAL PROBLEMS ENCOUNTERED BY CUSTOMS LABORATORIES. Robert E. Lang, U.S. Customs Laboratory, 201 Varick St., New York, N.Y. 10014

The Bureau of Customs has the mission of collecting revenue on imports and of enforcing the laws regarding controlled and prohibited exports and imports. The Customs Laboratories' major role is to conduct the necessary analyses to permit proper tariff classification and/or valuation on imports and to identify any controlled or prohibited items. Samples received by the laboratories for analysis are many and cover the entire range of imported merchandise. At the same time, the total manpower available to perform these analyses is relatively small while the extent of the analytical examination required for a given importation is variable as it is heavily influenced by the applicable provisions of the tariff laws and their interpretations by the courts. This combination of circumstances contributes to our operational problems as an analytical laboratory and makes it a necessity that we be constantly upgrading our staffs, our equipment and our methodologies. A full discussion is made regarding our overall analytical problems and the steps being taken to alleviate them. These are further illustrated by specific examples of typical problems encountered.

2. FDA ANALYTICAL PROBLEMS RELATED TO FOOD CONTAMINATION. Edward O. Haenni, Division of Chemistry and Physics, Food and Drug Administration, Washington, D. C. 20204.

The problems confronting regulatory agencies in controlling the quality and safety of the food supply have become increasingly complex with advances in food technology and with recognition of the influence of environmental pollution. Industrial chemicals (including toxic elements), natural poisons, pesticide and drug residues, reaction products of food additives, deleterious products of food processing, as well as newly developed foods from unconventional sources pose analytical problems of unprecedented sophistication to challenge the ingenuity of the food chemist. Specific examples and progress in their solution are discussed.

3. SOME RECENT USDA PROBLEMS IN THE IDENTIFICATION OF PESTICIDE RESIDUES AND CONTAMINANTS. J. R. Plimmer, Plant Science Research Division, Agricultural Research Service, U. S. Department of Agriculture, Beltsville, Md. 20705.

In agricultural research, there is an increasingly wide range of problems which must be solved by an understanding of phenomena at the molecular level. A problem of increasing concern is the identification of pesticide residues. Residues include not only the original pesticide but also the products of its chemical and biochemical transformations in the environment. We must understand the significance of these terminal residues, as they may persist in the environment, move from their site of application or injure some organism beneficial to man. Pesticide alterations in soil have been studied, since soil provides a route by which residues may contaminate air, water, and foodstuffs. An example is provided by the fate of aniline-based herbicides which may be converted to azobenzenes and many other products by soil or microorganisms. The problem of identification is also important in the case of pesticide contaminants. Some of these are potentially hazardous. For example, the chlorinated dibenzo-p-dioxins present in 2,4,5-trichlorophenoxyacetic acid and some chlorinated phenols. Combined gas chromatography/mass spectrometry and high resolution mass spectrometry have been used as identification techniques to supplement quantitative analysis by gas chromatography.

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in absorbance is linearly related to the water content up to 10 g/100 ml. A detection limit of 0.02 g/100 ml was obtained. It is postulated that the color change is due to keto-enol tautomerism, with the keto form being responsible for the green color in acetone and the enol form being responsible for the yellow color in water. The method is applied to the determination of water of hydration in lithium perchlorate.

8. ELECTROMETRIC TITRATION PROCEDURE FOR DETERMINATION OF AQUEOUS SOLUBILITY OF ORGANIC ACIDS AND BASES. W. W. Davis and C. J. Kreutler, Eli Lilly and Company, Indianapolis, Indiana 46206.

Many drugs are salts of acids or bases that have limited water solubility. When the soluble salts are titrated in aqueous solution, precipitation is encountered at some pH near the pK'a. If the titration is continued at a moderately slow rate through the insolubility range of pH, the acid binding curve follows a course that can be formulated and interpreted in terms of a solubility product. For an acid, $K^A_{sp} = [H^+]\cdot[A^-]$, or for a base, $K^B_{sp} = [H^+]/[BH^+]$. These solubility products can be used to specify the concentration of A^- or BH^+ that can exist in equilibrium with precipitated acid or base at any specific pH. The value of [HA] or [B] is constant when solid HA or B is present. A plot of the acid binding curve through the region of insolubility conforms to a calculated theoretical curve for acid bound - versus pH. The relationship for the titration of an acid is: $pH = \log (1-\alpha) - \log \frac{K_{sp}}{C}$. This curve is imprinted on a transparent mask and used for matching the experimental to the theoretical curve. K^A_{sp} or K^B_{sp} is obtained simply from a pH reading taken at $\alpha = 0.0$ or 0.5 from the experimental curve with the help of the mask.

9. ELECTROMETRIC TITRATION PROCEDURE FOR DETERMINATION OF THE OIL-TO-WATER PARTITION OF ORGANIC ACIDS AND BASES. W. W. Davis and C. J. Kreutler, Eli Lilly and Company, Indianapolis, Indiana 46206.

When a drug is titrated in the presence of a finely dispersed oil phase the free acid or free base distributes rapidly between water and oil. As the titration proceeds the dissociation equilibria in the water phase continue to fulfill the relations $K'a = \frac{[H^+][A^-]}{[HA]_w}$ and $K'a = \frac{[H^+][B]}{[BH^+]}$. The consequence of the proportionate removal of HA or of B into oil is a simple shift of the apparent pK'a by an amount which depends upon the ratio of the volume of oil to the volume of water and the oil-to-water distribution coefficient of the free acid or free base. A shift to higher pK'a occurs for an acid and an opposite shift occurs for a free base when an oil phase is present. Determination of the extent of shift of pK'a in the presence of a dispersed immiscible oil phase allows simple direct calculation of the distribution coefficient of the free acid $D^A_{o/w}$ or free base $D^B_{o/w}$: $D_{o/w}\cdot V_o = V_w$ (antilog Δ pK'a - 1). This in turn permits calculation of the partition of the drug at any pH by multiplying $D_{o/w}$ by the fraction of the drug in the free acid or free base form in the aqueous phase.

10. A SIMPLE CONTROL AND DATA LOGGING SYSTEM FOR BASE HYDROLYSIS OF ESTERS. K. M. Wellman, M. Lorusso, S. Zapico, R. W. Dively, T. Manning, Department of Chemistry, University of Miami, Coral Gables, Florida 33124.

We have constructed an electrochemical control and digital data acquisition system for monitoring first-order base-hydrolysis reactions spectrophotometrically or with sodium ion sensing devices. The basic system consists of a potentiometric controller and signal delay device for maintaining constant pH (±0.01 pH unit) in conjunction with an analog to digital converter and Kennedy magnetic tape recorder. The data acquisition system is capable of accepting 25 3-wire inputs which permits

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