MONSANTO CHEMICAL COMPANY
RESEARCH AND ENGINEERING DIVISION
RESEARCH DEPARTMENT
DAYTON, OHIO

Report On

Instrumental Analytical Conference

New Developments

Held at R&E Division, Dayton

June 22, 23, 1959

Distribution

R. Buchdahl - Springfield
T. Boyd - "
W. M. Lane - Texas City
R. L. Wall - "
G. Roberts - "
H. A. Ory - "
R. M. Munch - St. Louis
R. E. Keller - "
E. M. Emery - "
L. J. Spillane - El Dorado
S. Drexler - "
G. W. Steahly - Nitro
D. Guerry - "
R. Murie - Nitro
R. K. Flitcraft - St. Louis
J. R. VanWazer - "
D. P. Ames - "
C. F. Callis - "
T. J. Williams - "
L. Hellums - "
H. O. Hehner - "
E. W. Gluesenkamp/F. C. Meyer
R. L. Jenkins
W. T. Cave
D. R. Beasecker

This was the second meeting of Monsanto personnel representing the particular interests of instrumental analysis. The first meeting was held in Dayton in June 1957. Offers to act as host for the second meeting were received from Plastics Division (Texas City), Inorganic Division, (St. Louis) and R&E Division (Dayton). A majority vote selected both location and dates. The theme for the meeting was "New Developments" and the program was composed of papers volunteered by the divisional laboratories. Attached are copies of the agenda, attendance list and summaries of the papers.

After the dinner on Monday evening an interesting two hours were spent in discussing the possible scope and limitations of the proposed central analytical services for the additional research facilities to be located on the Creve Coeur campus. Mr. Wm. E. Weiner, Assistant Director Engineering Services and R&E representative on the Planning Committee was on hand to provide facts and figures as these were required. No attempt was made to reach unanimity although the pattern of comment was generally consistent and favorable. Being an informal part of the agenda, no notes were kept and no further report is planned.

Judging from the comments of the participants, the conference was highly successful in stimulating interest in and understanding of some of the more recent developments in analytical techniques.

W. T. Cave

INSTRUMENTAL ANALYTICAL CONFERENCE

"NEW DEVELOPMENTS"

Monday June 22 (Hochwalt Room - Bldg. 2)

8:30	Introductions and Program Notes	
8:45	VPC - Special Techniques	(Org.)
9:15	VPC - High Temperature	(R&E)
9:35	VPC - The Pye-Argon Instrument	(R&E)
10:00	Break	
10:15	VPC - Alkylbenzene Research	(Inorg.)
10:45	Chromatography - Liquid-Liquid	(Org.)
11:15	Chromatography - Evaluation of Paper Chromatograms	(Inorg.)
12:00	Lunch	
1:00	*M.S. - Low Ionizing Voltage	(Lion)
1:30	M.S. - Applications	(Texas City)
2:00	Particle Size Distribution	(Inorg.)
2:30	Magnetic Susceptibility	(R&E)
3:00	Break	
3:15	Electron Microscopy	(R&E)
3:45	Raman Spectroscopy	(R&E)
6:30	Visitors' Dinner at the Van Cleve Hotel	
8:30-10:00	Group Discussions	

* Not given

Tuesday June 23 (Hochwalt Room - Bldg. 2)

8:30	NMR - Introduction	
9:00	NMR - Phosphorus Compounds	(Inorg.)
9:30	NMR - Polymer Problems	(R&E)
10:00	Break	
10:15	EPR - Scope and Problems	(R&E)
10:45	XRF - Low Atomic Weight Elements	(Inorg.)
11:15	XRF - Matrix Problems	(R&E)
12:00	Lunch - Tours	
2:00	IR - Selected Topics	(Texas City)
2:30	IR - P-N Compounds	(R&E)
3:00	Break	
3:15	IR - Aromatic Amines	(R&E)
3:45	IR - Organo-Metallic Compounds	(R&E)
4:15	Summary Comments	

VISITOR'S LIST

for the INSTRUMENTAL ANALYTICAL CONFERENCE. June 22 and 23

Representative	Division	Location
Dr. Ralph H. Munch	Organic	St. Louis
Dr. Robert E. Keller	"	"
Dr. Edward M. Emery	"	"
Dr. Clayton F. Callis	Inorganic	"
Dr. Donald P. Ames	"	"
Dr. Horace Ory	Plastics	Texas City
Dr. Thomas Boyd	"	Springfield
*Mr. Sam Drexler	Lion Oil	El Dorado
Dr. Dave Guerry	Organic	Nitro
Dr. Richard Murie	"	"
Mr. Lloyd Hellums	R&E (Eng.)	St. Louis

* absent due to illness.

Participating from Dayton:

Dr. William T. Cave
Mr. Donald R. Beasecker
Mr. William S. Coakley
Mr. Ronald B. Coffey
Mr. F. Neil Hodgson
Mr. Thomas F. Page
Mr. John V. Pustinger
Mr. Thomas E. Reichard
Mr. William D. Ross
Mr. James M. Schlater
Mr. Ralph B. Smith

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SPECIAL TECHNIQUES - GAS CHROMATOGRAPHY - E. M. Emery

Programmed Temperature Details were given of the construction and operation of a chromatograph designed to control the variation of column temperature with time. Commercial instrumentation was also described briefly. The advantages of this technique were noted as:

a. rapid analysis of mixture of wide boiling range;
b. closer approximation to ideal band shape throughout;
c. reduced possibility of missing high boilers;
d. greater instrumental versatility - temperature changes especially.

Examples of these advantages were described for:

a. an n-paraffin mixture;
b. an intermediate fraction from biphenyl production;
c. cyclohexanol production.

Combustor Evaluation The advantages and difficulties involved in the use of a CuO combustor were described. For high temperature work, where thermistor sensitivity was a limiting factor, the combustor followed the chromatographic column. This method was tested on Tall-Oil Resin methyl esters. Base line drift was compensated by use of a blank column. For C/H ratios, the combustor preceded a column to resolve the CO_2 and H_2O produced. Known standards were used to calibrate.

Column Pre-conditioning Oven The construction and use of this unit were described. Advantages related to economy of both helium and time.

Analyses Using Special Techniques

a. Trace (1-2 ppm) Maleic Acid in Fumaric Acid Injection block temperature was found to be critical in controlling dehydration to anhydrides and this fact was the key to the analysis.

b. Stabilized Methyl Parathion Formulation A pre-column was used to obviate fouling of the main column by the methyl parathion in the analysis for diethyl sulfate and isodecyl alcohol in a 70% methyl parathion-xylene solution.

c. Low-boilers in Cyclohexanol Product Analysis required the detection of trace cyclohexane, cyclohexene and benzene in wet cyclohexanol. Backflushing was used to avoid taking an inordinately long time for the analysis. A tetrahydroxyethyl-ethylenediamine column was used to resolve the low boilers in 5 minutes and the cyclohexanol, which would have taken two hours to elute, was swept back out of the column.

d. Dichlorophenol Separation of p-chlorophenol from other dichloro isomers was found possible by use of a benzylbutyltetrachlorophthalate column.

HIGH TEMPERATURE GAS CHROMATOGRAPHY - W. D. Ross, presented by J. M. Schlater

Details of construction of the FM model 124 High Temperature Gas Chromatograph were described briefly. This instrument has been used at 400°C to analyze mixtures of three, four, five and six ring polyphenyl ethers. Unmodified C-22 Firebrick, 40-60 mesh, was found to be the most suitable packing for a four foot stainless-steel column. Asymmetry of the bands was not a serious defect for quantitative measurement. Stable modifiers at high temperatures (400°C+) are rare and chromatography in this temperature range will probably depend on unmodified substrates.

THE PYE-ARGON GAS CHROMATOGRAPH - J. M. Schlater

The performance of this instrument, which uses an ionization detector, was compared with that of the more customary thermal detector types. Particular advantages in resolution and increased scope were realized from the use of smaller samples and lower column temperatures. Examples of analyses which demonstrated these advantages were given as:

a. separation of the components of Aroclor 1242;
b. separation of the dichlorobenzene isomers.

Another difficult problem, the separation of monobasic acids, is now being examined on this instrument.

GAS CHROMATOGRAPHY IN ALKYLBENZENE RESEARCH - E. Eccles, D. Ames, S. Clark, R. Miller, C. Hemler, presented by C. F. Callis

The specially constructed thermal conductivity vapor phase chromatographic units were described and the operating conditions found to be optimum for alkylbenzenes were outlined. Comparisons were made of chromatograms of commercial alkylbenzenes. The contribution of this technique to research on alkylbenzenes was illustrated with the results of a study of processing conditions leading to an improved product with respect to color and oil.

Comparison was also made of the superior results possible with the new ionization detector - capillary column equipment over the conventional thermal conductivity units.

The all nylon block and thermistor detector used in studies of volatile, corrosive inorganic materials such as silicon halides was also described.

LIQUID-LIQUID CHROMATOGRAPHY - R. E. Keller

Apparatus and reagents were described; the applications of this technique to specific problems were explained; the scope and limitations of the method were indicated.

Apparatus It was found necessary to classify the silica gel to avoid fines and the amount of water associated with the silica gel was found to be critical. A Gilson UV asorption meter and fraction collector were used affectively to analyze the separation of components.

Problems

Phenol Process The evaluation of benzene disulfonic and related acids in benzenesulfonic acid was required. The separation was made with the barium salts of these components and measurements were made by ultraviolet absorption. The choice of eluting solvents was critical.

Adipic Acid The evaluation of lower dicarboxylic acids in mother liquors was required. In this case the chromatogram was followed by titration of the acid constituents of each fraction as they emerged from the column. (adipic, glutaric, succinic, and oxalic + nitric acids).

Fumaric, Maleic and Related Acids Analysis was required to obtain kinetic data for the isomerization of maleic to fumaric acid. Polarographic analysis was used to evaluate the chlorosuccinic acid which was not resolved from fumaric acid. Malic acid was positively identified by coupling with β naphthol and subsequent fluorescence analysis.

Phenol Process-Steam Fusion For the identification of by-products in the fusion step, ten milligrams of sample charge were partitioned between water and isooctane and the diphenyl oxide, o-phenylphenol, diphenylsulfone, p-phenylphenol and phenol that separated were measured by UV absorption. The amount of free water associated with the silica gel was critical.

p,p'-Bisphenol A The identification and quantitative analysis of impurities was desired. Chroman, phenol and o,p-Bisphenol A were separated by partitioning between water and 36% isooctane in chloroform.

In summary, liquid-liquid chromatography was suggested as a supplement to gas chromatography where the following features were significant:

a. inexpensive equipment;
b. gentle conditions - room temperature - noncatalytic equipment;
c. many fractions obtainable;
d. applicable to high-boiling compounds;
e. simple predictions of elution order - based on partition coefficients.

AUTOMATIC EVALUATION OF PAPER CHROMATOGRAMS - E. Karl-Kroupa and R. Kolloff, presented by C. F. Callis

The techniques of ion-exchange and paper chromatography used in the differential assay of phosphate mixtures were briefly reviewed. A detailed discussion was given of the recent adaptation of the Spinco "Analytrol" densitometer to the automatic evaluation of paper chromatograms for assay of phosphate-containing detergent compositions.

APPLICATIONS OF MASS SPECTROMETRY - H. A. Ory

Techniques of using the mass spectrometer, particularly in conjunction with the infrared spectrometer and the gas chromatograph, on analyses of unknown mixtures were discussed.

Steps in Qualitative Analysis were described as follows:

a. use of group peak patterns and parent peaks (paraffins, oxygenated compounds, nitriles);
b. molecular weight determination by diffusion through a gold leak, plotting peak intensity vs time;
c. reference to standard cracking patterns;
d. preliminary separation by gas chromatography and identification of single components;
e. use of the Artichoke computer program, where pre-separation by chromatography was not done, and the spectral contributions of the heavier compounds were "peeled off" to remove interference with spectra of lighter components;

f. chemical reactions - i.e. hydrogenation, to alter spectra predictably for peak identification;
g. use of low ionizing voltages to produce molecular ions and thus simplify the spectra.

For subsequent quantitative evaluations conventional techniques were described for the IBM 650 electronic computer. Up to thirty-five components have been analyzed routinely-detection limit 10-500 ppm - accuracy 1% relative on major components.

PARTICLE SIZE MEASUREMENTS - R. R. Irani and D. P. Ames, presented by D. P. Ames

The measurement of particle size distribution of powders in the subsieve range by the Flying Spot Resolver and an automatized Gallenkamp liquid sedimentation balance were outlined. The size distributions were shown to exhibit log normal distribution behavior. The results of the two independent methods were shown to agree with the predicted values based on transformations involving log normal distributions. The transformation of a number size distribution to a weight size distribution was outlined. The interpretation of abnormal log normal size distributions was indicated. An evaluation of particle size distribution measurements by sieves was made. The utilization of calibrated sieves (U.S. Screens and Buckabee Mears Micro Screens) was emphasized.

MAGNETIC SUSCEPTIBILITY MEASUREMENTS - T. E. Reichard

The basic theory and the application of the Gouy and Faraday methods were described. The Dayton (Gouy) apparatus was illustrated.

Procedures for obtaining, processing and interpreting data were discussed as follows:

a. the use of Wiedemann's law of additivity of susceptibilities for measurements on mixture and solutions;
b. the requirements for relative and absolute measurements;
c. the use of inter-property relationships of volume, mass and molar susceptibilities;
d. the calculation of permanent molar magnetic dipoles and the interpretation in terms of unpaired electrons;
e. the correction for ferromagnetic trace impurities employing diamagnetic contributions obtained by Pascal's atomic diamagnetic increments and making constitutional corrections;

f. the separation of diamagnetic and paramagnetic contributions by measurements over a range of temperature.

ELECTRON MICROSCOPY - T. E. Reichard

A brief review, with illustrations, was given of the following special techniques and problems:

a. the observation and use of crystal reflections;
b. the value and use of ultrasonic dispersion;
c. the manufacture and use of carbon replicas;
d. the evaluation of structure, fusion and poly-crystallinity of fine powder metal oxides produced by combustion;
e. the use of special methods for the preparation of silica sols (Syton 200) - freeze-drying, spraying, albumin coating of substrate and gelatin solution addition;
f. the analysis of copper-alumina rods by the correlation of results from optical metallography, EM replicas and XRD determination of preferred crystal orientation;
g. the extension of corrosion studies of glass fibers using a special surface-replica technique for very small objects and demonstrating the importance of orientation in shadowing and photographing replicas;
h. the study of fatigue failure of steel tubes using pre- and post-shadowed carbon replicas.

RAMAN SPECTROSCOPY - D. R. Beasecker

The instrumental details of the Cary 81 Automatic Recording Spectrophotometer were shown and described. A brief review of the theory of Raman scattering was given, showing the close relationship to IR absorption in the interpretation of data. Applications to specific problems were noted:

a. unsaturation - olefins and acetylenes;
b. branching - hydrocarbons (t-butyl groups);
c. sulfur bonds - identification;
d. ions - use of water as a solvent.

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NUCLEAR MAGNETIC RESONANCE - INTRODUCTION - W. T. Cave

A brief review of the instrumentation and basic theory were given covering the following:

a. resonant frequency = $\gamma \cdot H$;
b. signal strength $\sim N \times H^2 \times \gamma^3 \times I(I+1) \times T$;
c. multiplicity = $2nI + 1$;
d. chemical shift = $\frac{H - Hr}{Hr} \times 10^6 = \delta$ ppm;
e. spin-spin coupling.

NUCLEAR MAGNETIC RESONANCE-PHOSPHORUS COMPOUNDS - D. P. Ames, A. Wiesner and S. Ohashi, presented by D. P. Ames

The utilization of P^{31} nuclear resonance spectroscopic measurements to evaluate the type and amount of phosphorus containing species was illustrated by phosphate chain length measurements, pyrophosphite hydrolysis studies and the P_2O_5-HF-H_2O homogeneous equilibrium composition studies. The positional effect of sulfur on the chemical shift of organic phosphates, phosphites and phosphonates was used to illustrate simple structural effects. The interpretation of the nuclear resonance spectra through the use of perturbation methods was illustrated by the $PNCl_2 \cdot POCl_3$ addition product (AB type), sodium tripolyphosphate and $Na_5P_3O_8$ (AB_2 type) and P_4S_3 (AB_3 type). The utilization of spin decoupling as a structural aid was illustrated by the reduction of the ABX type spectrum exhibited by the diphosphite ion ($H\overset{O}{\underset{O^-}{P}}-\overset{O}{\underset{O^-}{P}}H$) to a simpler AB type spectrum.

NUCLEAR MAGNETIC RESONANCE-POLYMER PROBLEMS - J. V. Pustinger

The anomalous splitting in the proton resonance pattern for polystyrene and the copolymer styrene/methylmethacrylate 90/10 and 50/50 was shown and discussed. An explanation put forward by Bovey and Tiers "The Application of Nuclear Magnetic Resonance to the Study of Motion and Conformation of Polymer Chains in Solution" (ACS meeting, Boston April '59, Division of Paint, Plastics and Printing Ink Chemistry, p 148-155) was reviewed and the need for further data indicated.

ELECTRON PARAMAGNETIC RESONANCE-SCOPE AND PROBLEMS - W. S. Coakley

The basic theory was reviewed and the instrumentation described and explained. The following applications of this technique were discussed:

a. the detection of unpaired electrons (free radicals, transition element ions, "odd" molecules and triplet electronic structures);
b. the determination of the spectroscopic splitting factor "g" and thereby differentiation of types of paramagnetic materials;
c. the structural information available by analysis of the fine structure due to the interaction of magnetic moments of the electron and adjacent nuclei (2nI + 1). Experiments were described to show:

   1. the degree of sensitivity, by the detection of 10^{-6} moles of 1,1-diphenylpicrylhydrazyl;
   2. the formation of free radicals in polymers by irradiation (radioactive cobalt source).

X-RAY FLUORESCENCE MEASUREMENTS OF LOW ATOMIC WEIGHT ELEMENTS - E. F. Kaelble, presented by D. P. Ames

The analysis of chlorine in wheat flour and various wheat flour fractions and in treated wood were given as an example of the applicability of x-ray spectrographic techniques. The utilization of the x-ray spectrograph for the analysis of silicon as SiO_2 on surface treated paper and in antislip waxes was also discussed. The effect of the solids concentration on the calibration curve for bromine in salt water oil brines was given to illustrate the importance of matrix effects. The applicability of automatic x-ray spectroscopy for routine analyses of several elements was also discussed. Two instruments (Norelco's Autrometer and Applied Research's PXQ) capable of such measurements were described.

X-RAY FLUORESCENCE-MATRIX PROBLEMS - F. N. Hodgson

A fusion method for the preparation of samples as proposed by Fernand Claisse ("Accurate X-Ray Fluorescence Analysis Without an Internal Standard" PR No. 327, Dept. of Mines, Quebec, Canada, 1956) was discussed. By use of this method, errors due to differences in the Chemical composition of the Matrix, in grain size and in interatomic distances of the elements were eliminated. Data for the analysis of cobalt fortified iron oxides as obtained from the fusion method compared favorably with data from chemical analyses.

INFRARED SPECTROSCOPY - RECENT APPLICATIONS - H. A. Ory

A variety of uses of IR analysis were discussed:

a. the determination of the methyl/methylene ratio of low pressure polyethylene by the use of a differential technique which gave improved sensitivity for low methyl content samples;
b. the measurement of vinyl crotonate and vinyl butyrate in low concentrations to follow their rates of reaction with maleic anhydride in benzene, by the use of a differential technique;
c. the observation of a characteristic IR band at 11.8 μ when two chlorine atoms are bonded directly to the carbon atoms of the triazine ring;
d. the observation of specific absorptions due to the t-butoxy group - an extensive list is attached;
e. the study of aldehydes and ketones through measurement of the bisulfite addition compounds.

Current and future interests were noted:

1. solvent effects on IR intensities;
2. IR spectra of adsorbed molecules;
3. identification of fluorinated compounds;
4. structure of polypropylene.

INFRARED SPECTROSCOPY-PHOSPHORUS-NITROGEN COMPOUNDS - J. V. Pustinger

Data were described to establish the existence of the imido form, ($-P<^{O}_{NH}$), for ring compounds obtained by the hydrolysis of the phosphonitrilic chlorides. The use of anhydrous compounds and a melting technique were the means by which the >NH absorption in the 3300-2900 cm^{-1} region was identified for established chain compounds and then correlated to the ring compounds. Recognition of absorptions due to $>P\overset{O}{\leq}O$ - and $>P\overset{H}{-}N-P<$ linkages was assisted by the spectrum of deuterated potassium trimetaphosphimate. Characteristic frequencies were indicated for the $P-NH_2$ stretching and deformation for sodium, potassium, zinc, silver and thallium phosphoroamidates.

INFRARED SPECTROSCOPY-AROMATIC AMINES - T. F. Page, Jr.

A report was given on the results of studying the spectra of 70 primary and secondary amines and 100 derivatives.

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a. NH stretching - Two bands of almost equal intensity were found for large (> C_2H_5) substituents in the ortho position. Small ortho groups and m-p-substituents gave spectra showing three bands of unequal intensity.
b. -N-C(CH_3)$_3$ absorptions - Correlations were found for two bands, of almost equal intensity, occuring between 1400 and 1370 cm^{-1}.
c. >C-N< stretch - The presence of fine structure gave indication of useful correlations.
d. NH_2 deformation - This mode was found at ~745 cm^{-1} for the mono- and di-substituted amines and at ~770 cm^{-1} for the tri-substituted amines. The position of the band was affected by the mass of the substituent. The intensity of the band was increased as the basicity of the amine increased.
e. >C-H out of plane bending - Interfering N-H deformation absorptions were removed by preparation of acetyl or choroacetyl derivatives or the HCl or HBr salts. Characteristic aromatic ring substitution patterns were then observable.

Solid phase spectra frequently showed anomalous and misleading bands as compared to solution spectra.

INFRARED SPECTROSCOPY-ORGANO-METALLIC COMPOUNDS - R. B. Coffey

Complexes isolated from the reaction of iron carbonyl with diphenylacetylene were examined by IR to assist in structure identification. The main contribution came through the observation of ketonic and $\diagup M\text{-}\overset{O}{\overset{\|}{C}}\text{-}M\diagdown$ absorptions.

Thermal degradation of the complexes gave organic compounds (tetraphenylquinone, tetraphenyldienone, 1,2,3,4-tetraphenyl-1,3-butadiene) in the identification of which the IR spectra were of fundamental assistance.

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