

5. Quantitative determination of low boiling point phenols in phenolic oils by close fractionation.

Summary:

(1) The distillation of purified phenolic oil has been carried out in an 80 plate laboratory column under the described conditions and is a good procedure for the determination of carbolic acid, o-, m-, and p-cresol, with an accuracy of $\pm 2\%$.

(2) m-cresol is determined by nitration to the trinitro-product. The method has been tested and found useful for control purposes.

(3) The o-cresol determination is not reliable when the amount present is less than 50 g. in a distillation.

(4) If temperatures of 230°C. or higher are reached, the xylenols can also be determined, but not other phenols boiling in the same range (ethylphenols, o-, m-propylphenols, isopropylphenols, etc.).

(5) The determination of the solidification point of many close fractions is very helpful in effecting separations in the carbolic acid and o-cresol boiling ranges.

(6) It fails in the m- and p-cresol boiling range due to the same boiling point and the presence of a maximum melting point in the system p- m-cresol.

(7) The fractionation procedure gives only partial and uncertain results when applied to phenols from the Brux plant.

The report contains many distillation curves in the appendix.

This investigation was part of a hydrogenation research (Leuna Lab. 907) carried out from November, 1939, to February, 1940.

6. Report on a Conference on Molecular Spectra Held in Leuna on January 21, 1941.

The use of new alkylation processes required new analytical tools to determine the length and characters of hydrocarbon side-chains. A similar situation existed regarding the sulfochlorination process in which pure aliphatic fractions obtained from petroleum give, after treatment, mixtures of aliphatic and cyclic hydrocarbons. The use of the Smekal-Raman Effect and particularly the work of Goubeau (Bunsentagung 1940 and Phys. Chem. Kolloquium, Halle) appeared to offer the best solution of the problem and a meeting was called at Leuna to discuss the advisability of installing such apparatus and methods at Leuna. This meeting was attended by Drs. Timm and Stern from Oppau who were using the method,

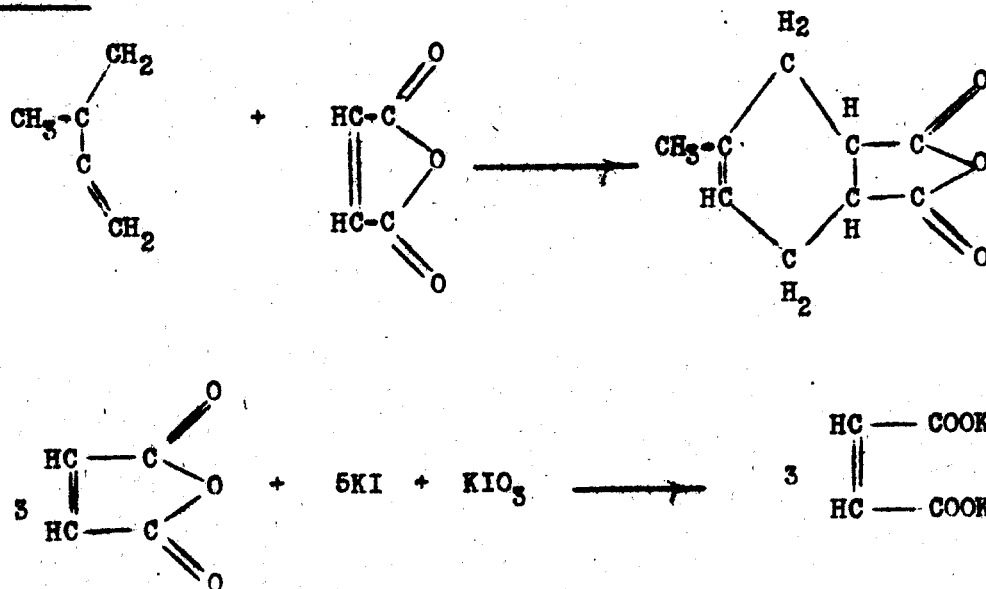
Dr. Timm explained the principles of the method and expressed the opinion that the technique should be very useful in clarifying the constitution of the higher molecular weight fractions of petroleum (C₁₂-C₁₈) in alkylation samples also on material resulting from the sulfochlorination of special hydrocarbons from petroleum fractions. These fractions consist mostly of molecules carrying cyclic systems in the side chains, and these rings are of especial interest. Dr. Timm felt that the Raman technique could also be used as control for close fractionations to enrich fractions with respect to a given hydrocarbon.

It was decided to adopt the technique at Leuna.

7. Isoprene Determination, Leuna, December 30, 1943.

The sample is dissolved in xylol and a known excess of maleic anhydride added. The mixture is left 10 hours at room temperature, gradually heated 3 hours until a temperature of 100°C. has been reached, then maintained 7 additional hours at 100°C. A known excess of KI and KIO₃ solutions is added, the mixture kept 2 hours in a dark place and the excess iodine titrated with $\frac{N}{10}$ Na₂S₂O₃. From the amount of iodine consumed, the amount of maleic anhydride consumed can be calculated, hence, the amount of isoprene present in the sample.

Reactions:



Pentane, isopentane, pentene, or isopentene do not interfere when the amount does not exceed 0.9 g. per analysis. Consequently, it is best to use small samples. C₄ olefins interfere since iodine adds to the double bond and maleic anhydride reacts at higher temperatures. C₄ saturates do not interfere. Accuracy ± 2%.

8. Research with a new indicator to replace Methyl Orange. Leuna,
December 7, 1936.

Methyl orange, when titrating an aqueous solution with an acid changes between pH 4.0 and 3.0 from yellow to onion-red and this change is difficult to observe when the original color of the solution is yellowish-brown. The new indicator to which attention has been called by K. Höppner in Deutsche Zuckerindustrie, 61st year, No. 16, is a mixed indicator. It consists of 4 parts of a 0.2% alcoholic solution of bromoresol green and one part of a 0.2% alcoholic solution of dimethylyellow. The color changes from blue through green to yellow. The change takes place at 4.7 pH.

The new indicator was found to be very satisfactory, particularly for titration of colored aqueous solutions such as crude boiler feed and condenser waters. Titration curves are presented.

9. Determination of bromine number in benzine and other olefinic solutions
(Leuna).

This procedure has been developed particularly for use in connection with unsaturate determinations on products resulting from the OKO process (addition of carbonyl groups to olefins) and is the only satisfactory procedure in the presence of aldehyde and ketones. It depends upon the fact that halogens react with double bonds at temperatures from -50 to -80° just as fast as at room temperature, while the velocity of the side reactions, particularly substitution, is greatly reduced.

The titration is carried out in a test tube held in a Dewar flask filled with dry ice and methanol. The bromine is added in chloroform solution the first permanent light yellow coloration being the end point. The following values have been obtained on various olefins:

	<u>Bromine No.</u>	
	<u>Found</u>	<u>Theoretical</u>
1-Hexylene	192	190
Cyclohexane	195	195
Diisobutylene	144.5	143
Polymer benzine fraction 95-98°	165	163 for C ₇ H ₁₄
Polymer benzine fraction 122-124°	137	143 for C ₈ H ₁₆

Aldehydes and ketones do not react. The reaction with diisobutylene is somewhat slower. Alcohols, sulfur compounds, aromatics, and hydro-aromatics do not react.

The procedure has been in use since the middle of 1940.

Comments: This procedure should be of great interest to U. S. laboratories in view of the large amount of work carried out in this country

by ASTM and others in attempting to develop a satisfactory procedure. So far, only empirical methods have been developed which allow for a considerable amount of substitution. The German procedure should be tried and the mixture after the end point back titrated in accordance with McIlkiney's method to determine if substitution has really been prevented.

10. New infrared method for gas analysis. Oppau, May 10, 1938.

The apparatus is shown in Fig. 1. A glowbar sends heat rays through an absorption tube to a receiver consisting of a thermocouple or receiver. If the absorption tube contains a gas, heat will be absorbed and the amount of heat received by the thermocouple will be lower. A measuring instrument attached to the thermocouple will give the amount of heat transmitted. Generally, a compensation arrangement is used consisting of 2 thermocouples, one of which registers the absorption of a standard gas. Such an arrangement compensates for any variation in intensity of the light source.

A complete description of the apparatus is given, including pictures of the absorption and registering apparatus. Spectral curves of CO₂, CO, ethylene, acetylene, methane, and ethane are attached.

11. Researches with the electron microscope. Oppau, June 6, 1938.

This research has been carried out to examine the surface of active catalysts. It has been shown that the present knowledge of electron optics can be used to advantage for such investigations. Three methods are available for surface examinations, namely, the light emission method, the light electric, and by ionic bombardment.

The light emission method is the most intensive but requires very high temperatures for pure metals, often above the melting point (above 1400°C.). However, this temperature can be substantially lowered by activation with an alkali or alkali-earth metal. This activation is carried out by producing a very thin layer over the surface of the metal to be examined. The layer must be so thin that the crystal structure and its modifications (recrystallization) can be seen in the electron picture. It lessens the disappearance of the electrons thereby lowering the emission temperature, for instance, that of nickel is lowered to 450°C. by the vaporization of cesium.

By the use of light, electrons can be emitted at any temperature even from pure metal surfaces. However, the number of these electrons is much smaller than emitted by the light emission method.

The electron bombardment method is not suitable for this work since it results in permanently modifying the character of the surfaces under examination.

It has been found that the light electric electron emission method is the most suitable for the examination of catalysts, since the light emission temperature is generally too high and the character of the surface is generally destroyed. It has also been found that the use of the latter procedure generally destroys the activity of the specific catalytic character of the surface under examination.

The research was carried out at the A.E.G. laboratories (German General Electric Co.), using one of their microscopes. The apparatus is fully described in the report. A summary of the report is given below.

An electron microscope has been built with magnetic lenses and molybdenum oven and used for this research.

The surfaces of nickel, silver, and copper have been activated with barium and examined.

Since these surfaces must not suffer any modification in character, the examination has been carried out by the light electric emission procedure. Contrast structural pictures can be obtained by the light electric emission procedure, only by using wave lengths near the long wave emission range, or with catalysts the surface of which has been poisoned whereby the foreign substance is preferentially adsorbed on the active portion of the surface. The low emission intensity of the light electric procedure is a disadvantage.

12. Determination of nitrogen in coals, tars, oils, benzines, and similar products, Analytical Laboratory, Oppau, October 10, 1938.

Summary:

A comparison of the Dumas, Kjeldahl-Messmann and ter Meulen (hydrogenation with a nickel catalyst) methods for the determination of nitrogen in coals, tars, oils, gasolines, etc., in amounts varying from 0.01 to several percent, has been made. Over one hundred analyses were carried out with many types of nitrogen compounds. The conclusions are as follows:

(a) On pure substances such as nitrocompounds, amines, sulfur, and amines containing chlorine, anilides, aminoacids, diazo- and azo-compounds, pyridine-, pyrrol-, and pyrazolone derivatives, the Dumas procedure, as an automatic micro-procedure, gave accurate results.

The ter Meulen method gives inaccurate results with only aminoacids and diazo-compounds; by using a nickel-magnesium catalyst (instead of the nickel asbestos) the nitrogen in high sulfure compounds, also compounds containing chlorines (i.e., thiourea, trichloracetamide) can be accurately determined.

The Kjeldahl method failed with the majority of pure substances tested (i.e., pyridine, pyrrol- and pyrazolone derivatives, aromatic nitro- and azo-compounds).

On technical products:

(b) For the determination of nitrogen in brown and hard coals, solid hydrogenation residues, etc., the Dumas automatic micro method is satisfactory. Satisfactory and generally higher results are obtained in one hour by the Dumas method, as compared with 5 hours for the Kjeldahl-Selenium procedure. An exception is shown by the so-called nitrated Pott coals, which give higher Kjeldahl values for nitrogen than obtained by the Dumas method. These lower values by the Dumas method are due to the partial volatility of adsorbed NO-compounds which are liberated without combustion by the steam of CO₂.

The hydrogenation method of ter Meulen cannot be used on coals (except for a special modification).

(c) The Dumas method gives too high results on heavy tars, pitches, and similar high boiling products, due to too rapid gasification and consequent inclusion of undecomposed gases with the nitrogen. Consequently, the ter Meulen method is preferable or, if the sample is not homogeneous or the nitrogen content is low, the Kjeldahl-Selenium method (which allows the use of much larger samples) can be used.

(d) The Dumas method is not satisfactory for tar oils, middle oils, and gasolines for the above reasons. In such cases, the hydrogenation procedure of ter Meulen, including a nickel-magnesium catalyst, has been found to be very satisfactory and is quite a good control method. Using 100 mg. samples and an automatic apparatus provided with clock work or a synchronous motor and double hydrogen feed, a determination can be carried out in one hour as compared with 5 hours, for the Kjeldahl method. The results are in close agreement with those obtained by the Kjeldahl-Selenium method.

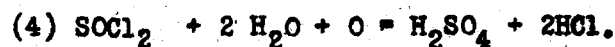
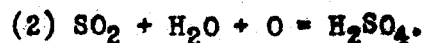
Comments: This is a very complete report on an excellent piece of research. The methods are well described, including illustrations and the procedure for the preparation of the nickel-magnesium catalyst. A long list of literature references is also given. This work indicates that laboratories carrying large numbers of nitrogen determinations on a variety of compounds should be prepared to use all 3 procedures if dependable results are desired.

15. The determination of Phosgene, Thionylchloride, Sulfurous Acid, Chlorine, and Sulfur Dichloride in the presence of each other, Ludwigshafen, May 2, 1943.

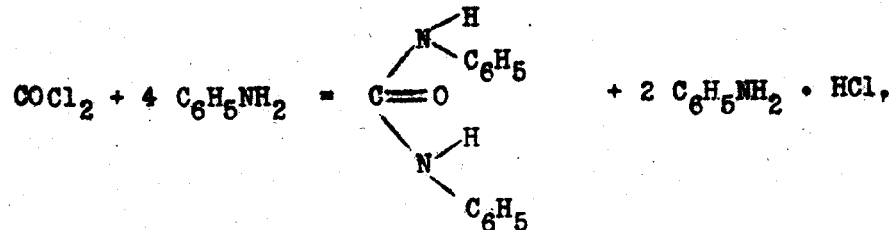
A crude product containing phosgene, sulfurous acid, chlorine,

and sulfur dichloride in solution is obtained in the manufacture of thionylchloride. The volatile impurities are driven off in the course of the purification and the resulting gaseous mixture contains, besides the above named impurities, also some thionylchloride. It was necessary to develop a rapid procedure for the analysis of this gas for control purposes. Such a procedure has been developed, based on the following considerations:

All these compounds are easily hydrolyzed by water, according to the following reactions:



The phosgene can be determined from the amount of CO_2 generated or by taking advantage of its specific reaction with aniline to symmetric diphenylurea according to the equation:



This determination can be carried out volumetrically (bromometrically). The total chlorine can be determined argentometrically.

The following determinations and calculations are made:

- pc - chlorine from phosgene (calculated from the direct phosgene determination).
- gs - total acidity (acidimetrically determined after hydrolysis in the presence of perhydrol).
- gc - total chlorine (argentometric determination after hydrolysis).
- su - excess SO_2 (direct determination).
- cs - chlorine as sulfur dichloride (direct determination).

ct - chlorine as thionylchloride.

gso - SO_4 formed by hydrolysis and the action of the present free chlorine on SO_2 .

fc - free chloride (equivalent gso).

fso - free SO_2

Then:

(1) $gc - pc - cs - fc = ct.$

(2) $gs - gc - su - cs = gso.$

(3) $gso = fc, \text{ then } gso \cdot 0.03547 \cdot 100 = \% \text{ free chlorine.}$

(4) $gc - pc - gso - 2 cs = ct, \text{ then } ct \cdot 0.0595 \cdot 100 = \% \text{ SOCl}_2.$

(5) $su + gso - ct - cs = fso, \text{ then } fso \cdot 0.032 \cdot 100 = \% \text{ SO}_2.$

(6) $cs \cdot 0.0515 \cdot 100 = \% \text{ SCl}_2.$

The various methods used which have been quite satisfactory are described in full detail, including a sketch of the absorption flask.

Comments: The mixture of compounds being examined is somewhat unusual and would not be met in ordinary oil technology. The methods are of interest nevertheless, at least for the determination of individual compounds.

14. Research on benzines of high olefin content, particularly on determination of the aromatic content. Open, June 1, 1939.

Table of Contents:

Introduction:

(1) Examination of the benzine for particular components,

(a) Ketones and their separation.

Separation as hydrazones.

Separation as oxime.

(b) Alcohols.

- (c) Esters.
 - (d) Peroxides.
 - (e) Conjugated dienes.
- (2) Determination of olefins.
- (a) The iodine No.
 - (b) Removal of olefins by the addition of BCl_2 .
 - (c) Riessfeld and Bandte procedure with 85-92% H_2SO_4 .
- (3) Determination of the sum of aromatics and olefins.
- (a) According to Lunge-Berl.
 - (b) According to Kattwinkel.

Modification of the Riessfeld and Bandte method.

- (4) Correlation of chemical and physical methods for determining the sum of aromatics plus olefins.
- (a) With aniline point according to Garner.
 - (b) Carry over of calculations from the Riessfeld and Bandte method.
 - (c) Search for an improved calculation procedure.
 - (d) From the density before and after chemical treatment.
- (5) Pure physical methods for determining aromatics.
- (a) Solvent power
 - (b) The Raman spectrum
 - (c) Evaluation of the refraction.

According to Watermann.

Our procedure.

According to Thomas, Blech, and Hoekstra.

- (6) Evaluation of the ultraviolet absorption spectrum.

Summary

The summary is translated below:

Several iodine No. procedures have been tested with samples high in olefin content (best, Huns or Meilinsky methods). For total aromatics plus olefins, a modification of the Riesenfeld and Bandte procedure is recommended (use of 50% H_2SO_4).

For the determination of aromatics the refractive index procedure gives results within $\pm 2\%$ (not sufficiently accurate) and only qualitative results for the naphthene content. The U.V. absorption is good for the determination of aromatics of the benzene series up to $C_{12}H_{12}$.

It is necessary to test unusual bensines for the presence of ketones, alcohols, esters, peroxides, and conjugated dienes. Peroxides must be absent in the determination of dienes by the maleic anhydride procedure.

Comments: This research should be of interest in view of the large amount of work carried out in the United States and elsewhere on the subject. The conclusions are in line with our general experience although iodine No. procedures are not favored for the determination of olefins in petroleum products, bromine No. procedures being preferred. The writer has no experience with the specific Riesenfeld and Bandte procedure, however, work in connection with ASTM has shown that generally poor results are obtained with the exception of a specific Kattwinkel reagent when applied to petroleum fractions of the gasoline end point.

The work has been carried out entirely on benzine fractions, no data on pure hydrocarbons being presented, with the exception of a table showing the depressing effect of some ketones on aniline point results. The chapter on ultraviolet absorption is well written and of definite interest. A rather novel (to the writer) procedure for removing peroxides is given. This consists of adding an alkaline, alcoholic solution of iron carbonyl until the filtered sample shows no further reaction. The excess iron carbonyl is then removed by shaking with H_2O and the precipitate filtered off. This procedure is preferred to the use of zinc dust, sodium bisulfite, active charcoal, hydrazine, or phenylhydrazine.

15. Determination of acetylene and hydrocarbons in liquid oxygen from

Table of Contents:

- I. Introduction.
- II. Quantitative determination of acetylene in liquid oxygen.

1. Principles and methods.
2. Experimental
 - A. Determination of acetylene in condenser and oxygen separator of the main apparatus.
 - B. Determination of acetylene in the krypton enrichment column.
3. Special directions.
4. Directions for the preparation of the solution.
5. Apparatus.

III. Quantitative determination of hydrocarbons in liquid oxygen.

1. Principles and methods.
2. Experimental
 - A. Determination of hydrocarbons in the condenser of the main apparatus.
 - B. Determination of hydrocarbons in the Krypton enrichment column.
3. Special directions.
4. Apparatus.

Attention is called (in the introduction), to the fact that air contains minute amounts of impurities such as saturated and unsaturated hydrocarbons, H_2S and nitrogen oxides. In the manufacture of liquid air, these higher boiling impurities condense (CH_4 - $161^\circ C.$, C_2H_2 - $84^\circ C.$, H_2S - $60^\circ C.$, and NO_2 - $10^\circ C.$) and will gradually concentrate into the liquid oxygen thus causing dangerous explosions. The determination of these impurities is therefore important from a safety viewpoint.

Acetylene has no vapor pressure at the liquid oxygen temperature. A large volume of the latter is therefore evaporated and the acetylene determined in the residue by the copper acetylide method.

Hydrocarbons are determined by evaporating a known amount of the liquid oxygen in a Dewar flask, scrubbing the gaseous mixture through an alkali solution, barium hydroxide and soda-lime to remove any CO_2 present. The scrubbed gases are then passed through a CuO tube held at $850^\circ C.$ and any hydrocarbon present will be burned as CO_2 which can be determined quanti-

tatively by scrubbing through barium hydroxide solution.

Full directions and apparatus sketches are given.

Comments: This report should be of interest to some of our foreign refineries who manufacture their own liquid air.

16. The determination of olefins and aromatics in hydrocarbon mixtures.
Oppau, April 7, 1941.

Table of Contents:

I. General

II. Determination of olefins in hydrocarbon mixtures.

1. Table of iodine Nos. of 10 olefins determined by 9 methods.
2. The platinum oxide catalyst and its action.
3. Determination of olefins in the presence of compounds containing carbonyl groups.
4. Research on the colorimetric determination of olefins with tetranitromethane (Dr. Fischer).
5. Description of the hydrogenation apparatus.
6. Determination of the hydrogenation number.

III. Determination of aromatics in the presence of olefins.

1. Research on the separation of olefins by sulfuric acid absorption.
2. Physical methods, combination of specific dispersion and hydrogen-iodine numbers.
3. Determination of specific dispersion.
4. Testing of physical methods.

IV. Summary:

The work is summarized as follows:

The best known iodine and bromine number procedures have been tested on 10 straight and branched chain olefins. None of the methods gave good results on all of the compounds tested.

A hydrogenation procedure using a platinum oxide catalyst gave excellent results with all compounds.

Aromatics are completely hydrogenated in the presence of the platinum oxide catalyst.

Mixtures of olefins and aromatics can be accurately analyzed; a combination of the hydrogenation number and specific dispersion permitting calculation of the aromatic content, and the hydrogenation - iodine numbers will give the olefins content. Tests on synthetic mixtures show that the method is satisfactory.

Comments: This work is of great interest since it bears on the important problem of determining the amounts of olefins and aromatics in liquid fuels. The authors appear to be satisfied with the results obtained although the error on the synthetic mixtures shown are somewhat larger than customary in analytical determinations. (Benzene added, 40.5%, found 38.0%; benzene added, 10.6%, found 8%). Since the data obtained with the hydrogenation method are much closer, it would appear that the above discrepancies must be due to errors inherent to the specific dispersion procedure. The hydrogen-iodine number is the iodine number calculated from the hydrogenation values.

17. Volumetric determination of very small amounts of sulfur in benzines, phenols, and leaves. Louma, April 10, 1941.

The samples are burned and the resulting gases scrubbed through hydrogen peroxide solutions. The SO_2 ion is then titrated with sodium rhodisonate used as an inside indicator. A known excess of 0.1N $BaCl_2$ is added and the excess of barium is titrated with ammonium sulfate, using sodium rhodisonate (tetraxyquinone) as an indicator, the color changing from rose to yellow at the endpoint.

Comments: The lowest sulfur values mentioned are 0.01% which would be high for aviation fuel. The method is not novel and the titration is not too easy to perform. Results compare favorably with gravimetric values.

18. Fluorine and silicic acid determination in cryolite. Louma, March 8, 1941.

The Stark-Hawley procedure for fluorine determination is preferred. This consists in fusing the sample with alkali carbonates in the presence of silicic acid. The filtrate from the melt is exactly neutralized and the fluorine is precipitated as $PbClF$ by addition of lead acetate. The washed precipitate is dissolved in nitric acid and the chlorine titrated by the Volhard method. Results compare very favorably with those obtained by the CaF_2 gravimetric procedure. The Oppau method of November 26, 1940, for the determination of free NaF in cryolite was tested and found to be

inaccurate. This procedure consists in extracting the cryolite with water, saturating the extract with ammonium sulfocyanide and sodium chloride and, after addition of alcohol-ether, titrating the fluorine with a ferric sulfate solution. Fluorine is precipitated in neutral solutions as FeF_3 and the first drop of excess ferric sulfate will give a red coloration with ferric salt, i.e., the endpoint. The difficulty is to obtain a truly neutral ferric sulfate solution, since FeF_3 is quite soluble when the least amount of acidity is present. In order to avoid the difficulty of preparing a neutral iron solution, an iron solution was titrated empirically with NaF. It was then found that the value of the titrating solution depended very largely upon the concentration, due to the strong solubility of the precipitate. A tabulation shows that the value of one ml. iron solution varies from 11.9 mg. NaF to 8.6 mg. depending on the concentration.

The method of Spielhaezek (Z. anal. Chem. 119, 1940 p. 4) for the determination of silica by fusing the sample with borax-bisulfate mixtures (whereby all the fluorine is expelled as BF_3) represents quite an improvement over the Jamaseh and Specht procedure.

19. Determination of sulfate in sulfonated detergents and wetting agents.
Leuna, December 4, 1941.

A review is made of the various known procedures for the sulfate determination in detergents and wetting agents. Methods previously worked out for Mesapon for the determination of sulfate were tested on other sulfonates. The rapid method by direct titration with BaCl_2 according to Hiltner is satisfactory for Mersolate of high and low sulfate content, low silica content wetting agents containing Mersolate, octadecylsulfonate (ampho soaps), arylsulfonate (Nekal) and fatty alcohol sulfates. The method does not give good results with Ipegon; carbonates, sulfites, and silicates interfere. The first can be removed by boiling with HCl before the titration, while there are no simple methods to remove the silica. The analysis can be carried out in 30 minutes.

The amyl alcohol method (shaking the sulfonic acids with amyl alcohol and precipitation of the sulfate in acidified solutions) will give satisfactory results if care is taken to use the proper size sample. The method can also be used for arylsulfonates (Nekal) and Ipegon.

Comments: There is an excellent review of the existing methods. A large number of determinations have been carried out on various samples with several procedures. The recommended method is new and of definite interest.

20. Research on phosphoric acid determination in catalysts. Leuna,
May 6, 1941.

The difficulty whereby only 60% of the phosphorus content is obtained by the ordinary analytical method when applied to used silica-zinc

oxide-phosphoric acid catalyst has been solved by fusing the sample with the mixed carbonates or preliminary HF treatment to remove the silica. It is concluded that the low results obtained by HNO_3 treatment are due to the presence of an insoluble silicium-phosphorus compound.

21. A new method for the oxidation splitting of ozonides, Leuna,
June 11, 1941.

Table of Contents:

I. General Section.

Introduction.

The possibility of producing acids by oxidation of olefins.

- (1) Oxidation with permanganate in aqueous medium.
- (2) Oxidation with permanganate in homogenous system.
(acetone solution)
- (3) Splitting of glycols according to Griegee.
- (4) Method of Prevost.
- (5) The Beckman rearrangement.
- (6) The method of Jegorow.

Ozonization of olefins.

- (1) Constitution of ozonides.
- (2) The possibility of rearrangement during ozonization.

The splitting of ozonides.

- (1) Boiling with water.
- (2) Oxidation splitting.
- (3) Reduction splitting.
- (4) Determination of formaldehydes as formic acid.

II. Research Section.

- (1) Oxidation of a higher molecular weight aldehyde to acids.

- (2) Splitting of an ozonide by the customary procedure of oxidation with H_2O_2 .
- (3) Oxidation of the same ozonide with an alkaline silver oxide suspension.
- (4) Oxidation splitting of the ozonide of a $\Delta 1$ undecylene.
- (5) Ozonization and oxidation splitting of cracked olefins from Ruhrchemie.
- (6) Splitting of fatty acid ozonides in pelargonic and azelainic acids.

III. Summary.

The customary procedures described in the literature for the production of carboxylic acids from olefins by the oxidation splitting of ozonides are not quantitative and cannot be used for the determination of the location of the double bond in olefin mixtures.

It has been shown that an oxidation splitting of the ozonide without side reactions taking place can be carried out by means of an alkaline silver oxide suspension.

The procedure has been patented.

Comments: This paper should be of possibly greater interest to organic chemists than to analysts. A novel method for the determination of formaldehyde is given as follows:

A small sample is weighed and dissolved into 10 times its volume of pentane and treated at $-20^{\circ}C$. with ozone until the excess gas liberates iodine from KI solution (with an efficient ozone generator the time should not exceed 10 minutes). When the reaction is completed, the pentane solution is added drop by drop to a silver oxide suspension in 5% NaOH solution, held at $40-50^{\circ}C$. The pentane will evaporate and is condensed. When all the pentane has evaporated, a reflux condenser is provided to the flask and the latter heated to $80-90^{\circ}C$. After standing 2 or 3 hours, the contents of the flask are transferred to a volumetric flask and an aliquot taken. The latter is acidified with dilute HCl, the precipitated silver chloride filtered off and the formic acid determined by the usual procedures.

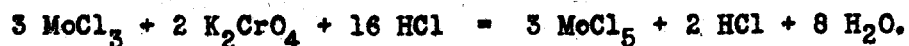
22. Potentiometric Molybdenum Titration, Leuna, June 30, 1936.

(Arch. f. Eisenhütten Wesen 8, 10:433, 1934/35)

According to the method of Klueger and co-workers, 1 g. of steel is dissolved in 1:1 HCl, oxidized with H_2O_2 and reduced with zinc. The

greater part of the molybdenum present in the steel will thus be converted to the trivalent form. The reduction of the molybdenum is then completed by treatment with chromium chloride according to specified directions. The resulting solution (the trivalent molybdenum, ferrous salts, and excess chromium chloride) are then potentiometrically oxidized with K_2CrO_4 . The potential curve shows, in the course of the titration, when the excess chromium chloride has been consumed, also when the oxidation of the molybdenum to the pentavalent form has been concluded. The difference between the two amounts of K_2CrO_4 solution consumed is equivalent to the amount of molybdenum present.

Reaction:



The oxidation as well as the reduction titrations must be carried out hot in the absence of air.

It is shown that the above procedure is quite satisfactory and gives results more accurate than obtained by the colorimetric method. As many as 20 determinations can be carried out per day if the total molybdenum and titanium can be reported together and no separation is necessary.

Results on known samples, also a diagram of the apparatus and titration curves are given.

23. Determination of available sulfur in polysulfide solutions.

Leuna, February 7, 1941.

"Available sulfur" was defined in Dr. Bankowski's report of Sept. 5, 1940, as the sulfur which will combine with the CN group to form CNS- or thiocyanates. Only thiosulfate and polysulfide sulfur need to be considered under this definition. Since the determination of thiosulfates does not present any difficulty, the report covers only the determination of polysulfide sulfur, for which no good methods were available at that time.

From the results, it is concluded that I.G. Method No. 239 (Kurtenacker's) for the determination of polysulfide sulfur gives outstandingly good results. The Bankowski procedure gives reproducible results; these results, however, do not correspond with polysulfide sulfur content only, but include a part of the thiosulfate sulfur (which is partly decomposed during the procedure) and can only be used empirically as an "effective" sulfur value.

The I.G. Method 239 is given in pages 9 and 10 which are missing.