I. SUMMARY

A. Plant visits were carried out while the war was still in progress and none of the German research analysts could be located for interviews.

B. It was found later by interviewing routine analysts that most of the research on analytical problems had been carried out by I. G. Farbenindustrie technicians at Oppau, Ludwigshafen, and Leuna.

C. A large amount of analytical documents have been evacuated and are being microfilmed.

D. The first microfilms have arrived in this country; these include both routine procedures and many research analytical reports.

E. Abstracts of the research reports and the writer's comments are given. The following reports are of special interest:

3. Analytical determination of gas mixtures, in particular those containing large amounts of gaseous hydrocarbons.

4. Volumetric determination of two olefin groups.

6. Report on a conference on molecular spectra.

7. Isoprene determination.

9. Determination of bromine No. in benzine and other olefinic solutions.

10. New infrared method for gas analysis.

11. Researches with the electron microscope.

12. Determination of nitrogen in coals, tars, oils, benzines, and similar products.

14. Research on benzines of high olefin content, particularly on determination of the aromatic content.

15. Determination of acetylene and hydrocarbons in liquid oxygen from the Linde apparatus.

16. The determination of olefins and aromatics in hydrocarbon mixtures.

19. Determination of sulfate in sulfonated detergents and wetting agents.

21. A new method for the oxidation splitting of ozonides.

25. Preparation, properties, and comparative capillary chemistry research on eight sulfonates and sulfates derived from hexadecane.

26. The volumetry of non-ideal gases. The mole volume of butadiene.

27. Comparison of various procedures for the determination of olefins.

28. The ultraviolet colorimeter, a control apparatus for the determination of phenol and other substances.

29. Analytical methods for Mersol, Mersolate, and wetting agents containing Mersolate.

30. Determination of very small amounts of carbon disulfide.

34. Method and apparatus for the water vapor determination in gases by means of calcium nitride.

35. The physical-chemical principles of extinction spectrography and its uses in visible and long wave ultraviolet light.

36. Efficiency of laboratory columns.

37. On the nature of the aromatic hydrocarbons present in pre-hydrogenation products.

38. Quantitative determination of ethylene oxide.
Research on the determination of xylenols by bromination.

41. Investigation on ketone oils.

44. Determination of benzoyl peroxide.

46. Analytical separation of hydrocarbon mixtures.
New methods for the isolation and identification of hydrocarbons in mixtures.

II. INTRODUCTION

Early in 1945 a group of petroleum and fuel technologists from both England and the United States investigated the present status of oil technology and research in Germany. This mission was carried out under the sponsorship of C.I.O.S. (Combined Intelligence Objectives Subcommittee) and with the cooperation of the British and American Armies in the European Theater of Operations.

The investigation consisted of: (1) examination of synthetic-oil, refining, and other plants related to production of petroleum products as previously outlined in a target list, (2) interrogation of German technical and administrative personnel connected with these plants, and (3) capture and examination of records, reports, and other documents relating to this industry.

As a member of this mission, the writer's duties were generally similar to those of other members, i.e., investigation of plants and laboratories, but particular attention was paid to analytical chemistry which happens to be the writer's field. It is well known that great advances have been made in this field during the war in the United States, particularly on hydrocarbon analysis, and it was felt that possibly the Germans may have made similar discoveries and even developed new procedures, which may be very useful and might lead to further advances in our oil technology.

III. PERSONNEL INTERVIEWS

The writer, having been in the field since the middle of March, 1945, hence while the war was on, found practically no analytical personnel to interview. This was likely due to the fact that some were hiding and the majority had retreated with the German forces still fighting. Moreover, most of the analytical laboratories seemed to have borne the brunt of the bombing, helping in the general dispersal of the staff. One chief analyst was found, Dr. Thies of the Chemische Werke Essener Steinkohle, A.G. at Kamen (near Dortmund, Ruhr), a Fischer-Tropsch plant. Dr. Thies was found to be quite cooperative and answered questions freely. The plant had been fearfully bombed, and there was only part of the gas laboratory left. With the exception of some of the most important papers, which were found in an air raid shelter, practically all records had been burned during the raids and the rest destroyed by liberated slaves three or four days before our visit.

Answering questions, Dr. Thies stated that his staff numbered about 100 when the plant was operating at capacity. His organization did no analytical research, (all such work being done by I.G. technicians at Oppau, Ludwigshafen, and Leuna) its functions being only for plant control. The laboratory procedures had been completely destroyed, but he admitted

that he had copies of his own at home and produced them the next day. These methods, which were developed at Oppau, were included amongst the documents collected at the plant.

The statement made by Dr. Thies regarding analytical research was corroborated by other technicians in several other plants. It was also pointed out that the bombing for the past one and a half years had been so severe and so continuous that all available technical help was needed to keep plants in operation and that no research work could have been carried out with any degree of continuity.

The writer also talked to Dr. Krüger, Chief Analyst, Dr. Eng. H. Braucker, (in charge of the gas laboratory), and Dr. Lehmann (in charge of the optical laboratory) of the Hüls (Ruhr) synthetic rubber plant. This plant, which was not listed as an oil target, was nevertheless visited by the writer, who had heard that some analysts were still around. The plant, which was well camouflaged, had been comparatively little damaged except for the analytical laboratory which was partly destroyed. The gas laboratory had not suffered much.

Dr. Braucker stated also that all analytical research had been carried out by the I.G. Hüls which was using the Leuna method, a procedure similar to the Shepherd Porter, for hydrocarbon analysis. He had one manually operated Podbielniak column. The Leuna method requires four hours for a C_4 cut separation and six hours for the cut analysis. Total unsaturation is determined with bromine water and isobutylene with 70% H_2SO_4. Sulfuric acid and silver sulfate is a reagent also used for this determination. Maleic anhydride is used for the determination of butadiene. The method used for the analysis of the fixed gas cut is of interest. Oxygen free nitrogen is used for flushing the pipettes. This is prepared by bubbling the nitrogen through water containing yellow phosphorus. Unsaturates are removed with bromine water, the hydrogen and CO are determined by combustion at 270°C. over copper oxide, and the remaining hydrocarbons (CH_4 + C_2H_6) by burning over copper oxide at 750°C. Total time, one hour, as compared with two hours for the Burrell apparatus.

The optical laboratory, which was untouched, was used for routine control. There was a Zeiss nephelometer, a Zeiss infra-red, and a Zeiss emission spectrograph. The infra-red technique was used entirely on C_4 analysis, the basic physical data being obtained from Oppau. No C_5 analyses were carried out, but much work had been done on diacetylene which could be determined by either ultraviolet technique (bands at 2430, 2315 Å) or gravimetrically with either silver or copper nitrate. The emission spectrograph was used for determining impurities in metals, catalysts, and water. Methods have been worked out for the determination of the following elements in comparison with the following lines of the iron spectrum:

Element	Wave Length Å	Iron Line Å
Vanadium	3110	3083
Molybdenum	2896	2828
Chromium	2677	2689
Nickel	3474	3399
Copper	3274	3287
Manganese	2933	3062

Methods for gas analysis also the diacetylene absorption spectrum were obtained and included with the documents collected at Kamen.

A visit was also made at the Kaiser Wilhelm Institute für Kohlenforschung, at Mulheim. Dr. Koch, who carries out whatever analytical work is necessary, stated that he had tried two procedures for the separation of α- from β-olefins, both being satisfactory. The first method (by peracetic acid oxidation) was developed by Boseken and Sturman, Rec. Trav. Chim. Pays-Bas, 56, 1034 (1937). A better and quicker procedure is by the use of mercuric acetate in glacial acetic acid. The α-olefins form a compound and give a lower layer, while the β-olefins remain in the upper layer. In the second step of the treatment with mercuric acetate, the upper layer is contacted and a new lower layer is obtained. This time it contains the β-olefins. The treatment is carried out at room temperature. A complete description is given in documents evacuated.

IV. PLANT AND LABORATORY VISITS

The following plants were visited. With the exception of Hüls, the analytical laboratories were either completely destroyed or had been so well evacuated that only empty benches were left.

1.	Oppau	I. G. Laboratories
2.	Ludwigshafen	I. G. Laboratories
3.	Gelsenkirchen-Nordsen (Ruhr)	Gelsenberg Benzin A.G.
4.	Scholven-Buehr (Ruhr)	Hydrierwerk Scholven A.G.
5.	Bottrop-Welheim (Ruhr)	Ruhr Öl A.G.
6.	Castrop-Rauxel (Ruhr)	Klocknerswerke A.G.
7.	Kamen-Dortmund (Ruhr)	Chemische Werke Essener Steinkohle A.G.
8.	Mülheim (Ruhr)	Kaiser Wilhelm Institute für Kohlenforschung
9.	Duisburg (Ruhr)	Gesellschaft für Teerverwertung
10.	Sterkrade-Holten (Ruhr)	Ruhrchemie A.G.
11.	Witten (Ruhr)	Deutsche Fettsäure Werke
12.	Amsterdam (Holland)	Bataafsche Petroleum Maatschappij
13.	Balingen (Wurtemberg)	Shale plants
14.	Autun, St. Hilaire, Severac (France)	French Shale Plants
15.	Salzgitter, Reelkirchen, Germany	Ruhrchemie A.G. (Documents)

Generally speaking, the analytical laboratories appeared to be well situated (too well!) with regards to locations in the plants. They are very spacious, a fact which American institutions could well afford to remember.

V. DOCUMENTS

Very large quantities of documents were evacuated. These were very roughly sorted in the field or at night at the billets (when light was available), then sent to London. Most of these documents were obtained from directors' or from chief engineers' or chemists' offices. While the writer did a great deal of document sorting in the field, careful reading could not be done at any time, due to lack of time and facilities. Many bags have not yet reached the base at London where the contents are being microfilmed.

Some of the microfilms have just arrived in this country and the writer has had the opportunity to view one reel with many analytical reports. These reports have been abstracted in the attached pages and the writer's comments follow some of the summaries. In view of the fact that these abstracts represent only a small portion of the total available information, this report is only a beginning and will be supplemented by a number of additional reports when the microfilms will have been received. There will be, in addition, a large volume of routine procedures which are of considerable interest and should be translated later.

VI. ABSTRACTS OF ANALYTICAL REPORTS FROM OPPAU, LUDWIGSHAFEN, AND LEUNA

1. Analytical determination of ammonia, mono-, di-, and trimethylamine. Leuna, September 30, 1932.

A method for the determination of mono-, di-, and trimethylamine in the presence of large amounts of ammonia (80-90% by weight) has been worked out. It was first necessary to increase the concentration of the methylamines. This is carried out by absorbing the gaseous mixture in methanol saturated with HCl, whereby 3/4 of the ammonia is precipitated out as NH_4Cl, the remainder and the methylamines remaining in solution in the methanol as hydrochlorides.

Three methods were tried for the analysis of the hydrochloride mixture: (1) I.G. Method 413, (2) a method recently developed by Dr. Fleming at Oppau, and (3) the Briner and Gandillon procedure. Method 3 has been selected as best and gave results within 1% of the true values.

The Briner and Gandillon method is described in Helvetica Chimica Acta, Vol. 1, XII, 1931, page 1283.

2. Research on the determination of impurities in electric arc acetylene by fractional distillation. Leuna, December 29, 1933.

A distillation procedure has been worked out for the determination of impurities in acetylene produced by the action of the electric arc on methane. The presence of ethylene, ethane, propylene, propane, allene, allylene, C_4 hydrocarbons, vinylacetylene, diacetylene, and some hydrocyanic acid was detected.

The distillation is carried out in a Leuna column which it is claimed is as efficient as a Podbielniak column. (Wustrow Merseburger Bericht, Vol. 5, 4, 1933). Synthetic mixtures were prepared at Leuna and subjected to fractional distillation. The operation was carried out at 30 mm. pressure. The data show that the mixture can easily be separated, the only difficulty being the separation of vinylacetylene from diacetylene. Results and distillation curves are given, including the vapor pressure curves of the pure hydrocarbons. The identification of individual components was not always too easy. This was carried out by determining physical properties such as vapor pressures and densities (Stock-balance). These determinations were carried out (in fractions containing more than one individual components) before and after removing olefins also before and after removing acetylenes by copper-ammonium solutions.

3. Analytical determination of gas mixtures, in particular those containing large amounts of gaseous hydrocarbons. Leuna, April 5, 1933.

This report is divided into the following sections:

A. Short introduction and description of the present apparatus for gas analyses.

(1) Drehschmidt apparatus for the analysis of hydrocarbon free (?) gas mixtures.

(2) Stock apparatus and method for the distillation and closed fractional condensation for the separation of gas mixtures.

(3) Method for the separation of gas forming hydrocarbons by fractional distillation in a column apparatus.

B. Description of improvements in the column apparatus.

(1) Apparatus modifications.

(2) Apparatus and procedure.

(3) Test analyses.

C. Summary.

A (1) Drehschmidt apparatus for the analysis of hydrocarbon free gas mixtures.

When an exact analysis of a mixture of gases is required, the Drehschmidt apparatus is generally used. As is well known, a measured volume of the gas is passed through KOH to remove CO_2 (the presence of H_2S and SO_2 requires special methods), then in the phosphorus or chromous chloride pipette to remove oxygen. The H and CO are then determined by fractional combustion at 270°C. over CuO and the CH_4 at 700°C., while nitrogen remains in the gas.

When higher hydrocarbons are present in the gas, the unsaturates are determined by absorption in a bromine pipette, before the oxygen determination while the higher saturated hydrocarbons are burned with the methane. The amount of methane can only be determined with accuracy when the higher saturated hydrocarbons consist only of ethane.

Consequently, the Drehschmidt apparatus will give only the total amounts of unsaturated and saturated hydrocarbons (unless the latter consist only of two components, i.e., methane and ethane). Moreover, the presence of higher hydrocarbons will affect the accuracy of the results since errors are introduced by the increased solubility of these compounds into the reagents, also some decomposition will take place in the 270°C., heated copper oxide tube, thus giving higher CO values.

For these reasons, in our laboratories, only those gases which are free from higher hydrocarbons are analyzed by the Drehschmidt apparatus. When present, these higher hydrocarbons are separated by condensation. When it is only necessary to know the total volume of the hydrocarbons present, only one volume measurement is necessary. Generally, however, the total amount of unsaturates and saturates are required. For such purposes, we have used, until very recently, the Stock distillation method with fractional condensation in the Stock high-vacuum apparatus. This procedure allows the separation of H_2, O_2, CO, CH_4, and N_2 from liquid hydrocarbons condensed by means of liquid nitrogen. The condensate is then slowly gasified into receivers held at various constant temperatures (C_5 and higher in -100°C. bath) butane (-125°C. bath) propane and propylene (-150°C. bath) and finally the C_2 hydrocarbons are also condensed. The accuracy of the separation depends upon the accuracy of the bath temperature (tolerance ± 2%).

The various fractions in the individual baths are then gasified and the total unsaturates determined with bromine water. Final control is made by determining the molecular weight with the Stock balance; the

error should not exceed ± 5% calculated on the hydrocarbon. The Stock procedure gives best and quickest results when the amount of condensate in each bath is not too large. Fractions larger than 100 cc. gas must be reduced. This is objectionable since with mixtures rich in higher hydrocarbons, it is often difficult to obtain sufficient sample for a Drehschmidt analysis.

To overcome this objection, a column apparatus has been devised which gives satisfactory results (?). (Accuracy ± 10% on individual hydrocarbons). Description and drawing of the apparatus are given, also distillation curves.

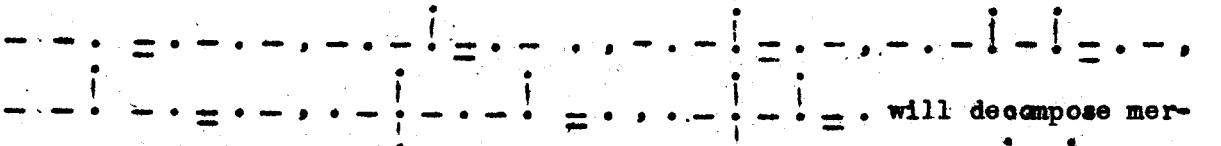
Comments: The first section has been translated in full since it gives a good picture of the gas analytical methods used by the Germans. The Leuna procedure seems to be generally used in other German laboratories. It is similar to the Shepherd-Porter method which has been superseded by the Podbielniak distillation in the United States.

Attention is called to the Drehschmidt procedure, particularly the final CuO combustion at 700°C. The laboratories at Castrop-Rauxel and also Scholven used a temperature of 750°C. Both laboratories, also Gelsenberg, claim a total time of 40-60 minutes for a complete analysis which compares very favorably with the two hours generally required by using the Burrell apparatus and the slow combustion pipette.

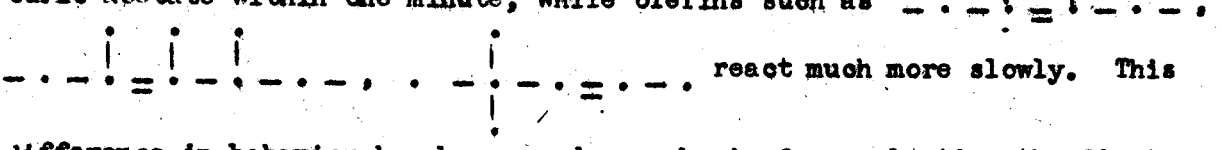
4. Volumetric determination of two olefin groups, Leuna, March 28, 1939.

This procedure is based on the Tautz method, whereby the olefins react with mercuric acetate, liberating an equivalent amount of acetic acid which can be titrated.

It has been found that olefins of the following configuration



will decompose mercuric acetate within one minute, while olefins such as



react much more slowly. This difference in behavior has been used as a basis for evaluating the first olefin group. The method is quite useful for determining the purity of an olefin. Curves showing the reaction times of olefins with mercuric acetate are given.

Comments: This procedure is of interest and should be tested on C_6 olefins.