ITEM IV

The material in this item has been taken from the files of the Oppau Laboratory of the I. G. Farbenindustrie. Because of the frequent reference between this and the Ludwigshafen Laboratory (see Item III) it is apparent that there is close administrative liaison between the two and great similarity of testing procedure was only to be expected. In fact, except for a few pages describing the construction of micro equipment and methods for determination of C, H, N, and S which are published in Micro Chemie and Zeitschrift fur Analytische Chemie, the greater portion of this item deals with analytical methods used with the high-pressure hydrogenation plants at Ludwigshafen and Oppau.

Since all of the material in this item has either been published or discussed in the review of earlier items, only one abstract has been prepared and the remainder marked as no value or published.

CODED INDEX

Sub-Item No.	Title	No. of Pages
	Asphalt (no value)	
	Engler distillation (no value)	
	Softening Point (published)	
	Sieve Analysis of triturated coal	
	Paraffin in Oil (published)	
	Melting Point of Paraffin (no value)	
C.	Analytical method for examination of coal stripper products	23
	Water (no value)	
	Specific gravity (no value)	
	Engler distillation (no value)	
	ASTM distillation (no value)	
	Aniline Point (no value)	
	Unsaturates (no value)	
	Phenol (no value)	
	Small scale examination of coal stripper product (no value)	
	Large scale examination of coal stripper product	
	H_2S in stripper water (no value)	
	NH_3 in stripper water (no value)	
D.	Analytical methods for examination of residue (Abschlam)	8
	Specific gravity (no value)	
	Softening point (no value)	
	Asphalt content (no value)	
	Viscosity (no value)	
	Filtration time (no value)	
E.	Analytical methods for the examination of gasoline	50
	Specific gravity (no value)	
	Engler distillation (no value)	
	ASTM distillation (no value)	
	Phenol (no value)	
	Loss on treatment with H_2SO_4 (no value)	
	Copper dish test (no value)	
	Glass dish test (no value)	
	Doctor test (no value)	
	Unsaturates (no value)	
	Analysis for hydrocarbon types (no value)	
	Refractive index (no value)	
	Small amounts of phenol (no value)	
	Air jet gum (no value)	
	Sulfur in oil and gasoline (no value)	
	Chlorine in gasoline (no value)	
	Reid vapor pressure (no value)	
	Octane number (no value)	
F.	Analysis of gases (no value)	51

ABSTRACTED AND TRANSLATED SUB-ITEMS

1. Determination of Nitrogen in Coal, Tar, Oils, Gasoline, etc. (Abstract)

In the determination of small proportions of nitrogen in coal, tar, oils, gasoline, etc. considerable discrepancies have been encountered among different laboratories depending on the method used. Therefore an investigation has been made on a comparative basis of the following three methods: (1) The Dumas method which is considered the standard method and is applicable to the determination of nitrogen in any form (certain proteins excepted). (2) The Kjeldahl method, originally designed for agricultural chemical analyses but which by the use of certain catalysts has become a generally applicable method. (3) The method by ter Meulen which is based on the hydrogenation of the nitrogen compound on a nickel catalyst to ammonia.

The analysis is concerned with the determination of nitrogen in proportions of a few hundredth of one per cent to several per cent in materials such as hard and soft coal, thick tar, heavy oils, heating oils, middle oil, kerosine, lubricating oils, extracts and residues from hydrogenation of coal, gasolines, waxes, gum, etc.

I. Dumas Method. At Oppau the method is used as semi-micro method using sample weights of about 200 mg. The burner for vaporization of the sample is moved either by hand or mechanically. With coal and similar solid materials the vaporization could be controlled in such a manner that reliable results were obtained, however, with tars, oils and similar materials difficulties arose. Frequently, in spite of very slow vaporization, it could not be avoided that the combustion proceeded too rapidly and in this way methane, carbon monoxide etc. passed with the nitrogen into the azotometer, therefore mechanical vaporization gave higher results than in case of careful operation by hand. The Dumas method failed completely in the determination of nitrogen in gasolines and similar low boiling samples, the combustion being too rapid so that too high results were obtained.

II. Kjeldahl Method. For the comparative study a catalyst of the following composition was used: 90 g. sodium sulfate, 7 g. mercuric oxide, 1.5 g. copper sulfate and 5 g. selenium dust. The procedure was as follows: 1-2 g. of sample are mixed in a 200 ml. Kjeldahl flask with a pinch of crystalline phenol and 2 g. of the catalyst mixture and 25 ml. of concentrated sulfuric acid is added. The flask is placed on a steam bath for one hour and then heated over an open flame until the sulfur acid is clear yellow. Heating is contained for another two hours and after cooling the usual distillation is made; range of measurement with 2 g. sample about 0.01% N.

III. Ter Meulen Method. A review is given of publications from which it was concluded that the method would be applicable. However, since the materials to be analyzed could contain frequently larger amounts of sulfur (also halogen) and the tube filling could not be renewed after each analysis, a nickel catalyst had to be used which was resistant to poisoning so that

it could be used for at least 15 determinations with one tube filling. As a suitable catalyst a nickel-magnesium catalyst was found, the so called "methane catalyst". It was also found advantageous to work with a double stream of hydrogen; the material is vaporized in one of the streams and the other stream carries the vaporized substance over the catalyst. Otherwise the apparatus and procedure is essentially that of ter Meulen. After the combustion the catalyst tube has to be kept filled with hydrogen. The catalyst is renewed after 15 determinations. Preparation of nickel catalyst, (Ni:Mg = 2:1) 1.23 Kg $Ni\,SO_4 .7\,H_2O$ are dissolved in 1.3 l. of water and 1.06 Kg $MgCl_2 .6\,H_2O$ in 0.45 l. of water at 40°C. To this mixture warmed to 60°-80°C a hot solution of 1.5 Kg Na_2CO_3 in 3 l. water and filtered over glass wool is added with constant stirring. The precipitate is allowed to settle and decanted several times, and then filtered through a Büchner funnel and washed until no longer reaction of chloride and sulfate in the filtrate. The precipitate is spread on filter paper, air dried and finally in vacuum at 100°C. After breaking up into about 7 to 8 mm. large pieces and screening, the small pieces are reduced in a current of hydrogen at 300-500°C, using an electric oven.

From the results of the analyses on various nitrogen containing pure compounds by the three methods the following summary is given: The Dumas method gives correct results, with the ter Meulen method only in case of amino acids too low results are obtained; the Kjeldahl method fails with the majority of compounds analyzed, particularly with pyridine, pyrrol, and pyrazolone derivates a.o. A large number of results are reported on, 1) technical products and mixtures of known composition, 2) on gasolines, coal tars, middle oil, kerosenes, residues etc. 3) on samples of coals; the results on coals were obtained by the Dumas and Kjeldahl methods only, and 4) on miscellaneous products such as fatty acids, gums, and waxes.

Summary.

The following conclusions have been reached: 1) with the analyzed pure substances (nitro compounds, amines, sulfur and chlorine containing amides, anilides, amino acids, diazo and azo compounds, pyridine, pyrrol and pyrazolone derivatives a.o.) the Dumas method carried out as an automatic micro procedure, gave correct results. With the ter Meulen method only in the case of amino acids and diazo compounds incorrect results were obtained. The use of a nickel magnesium hydrogenation catalyst allows the accurate determination of nitrogen in compounds with high sulfur and chlorine content, (thiourea, trichloracetamide).

With regard to the appropriate application of the individual methods to the mentioned technical products the following can be said: 2) For the nitrogen determination in hard and soft coal, solid residues from hydrogenation and similar products the Dumas method, used in the form of the automatic micro method, can be recommended, it gives within one hour (as compared to 5 hours by the Kjeldahl method) satisfactory values which on the average are higher than the Kjeldahl-selenium results (an exception are the nitrated pott-coals which by Kjeldahl method give more nitrogen than by the Dumas method. The reason apparently is the volatility of the loosely bound NO compounds which volatilize on passing CO_2).

The hydrogenation method according to ter Meulen is not applicable to coal (or only by using a specially modified procedure). 3) In the nitrogen determination in thick tars, in salve and pitch-like residues and similar high boiling products, the Dumas method usually gives too high values because frequently gasification takes place suddenly. In this case the nitrogen determination is made according to ter Meulen. Because of the usual non-homogeneity of this type of sample it is advisable to use larger sample weights (1-2 g.) and to make the determination by the Kjeldahl method. 4) For nitrogen determination, in tar oils, middle oils and gasolines the Dumas method is not applicable for reasons mentioned above. For the analyses of such samples the hydrogenation method according to ter Meulen with the Ni-Mg catalyst is suitable. Using sample weights of approximately 100 mg. the determination can be carried out easily in one hour by using an apparatus which is automatically operated with a synchronous motor. The values obtained by the ter Meulen method agree with those obtained by the Kjeldahl method.

Reviewers Observation: The two principle difficulties experienced in the application of the Dumas method to volatile hydrocarbons, both contributing to high results, confirm results obtained in the reviewers laboratory. In both instances, a means of circumventing these difficulties have been found to be so simple and effective as to nullify the above writer's conclusions as to the limitations of the Dumas method. The first difficulty lies in volatilizing the sample uniformly; this results in the carry-over of hydrocarbon gases later measured as nitrogen. The second difficulty comes about in the formation by cracking during combustion of hydrocarbon gases which are then measured as nitrogen. To control irregular volatility, the sample is volatized by means of a bare resistance wire wound directly on the combustion tube; control is effectively maintained by means of a variable transformer. Use of a piece of dry ice or an air stream over the sample container in the combustion tube facilitates control of very "wild samples". To remove hydrocarbon gases from the azotometer gas, it is mixed with excess oxygen and recirculated through the combustion furnace. By use of suitably designed apparatus the azotometer gas may conveniently be recycled several times to confirm complete combustion of all hydrocarbons. By this system, the Dumas method becomes very accurate in determining nitrogen contents of hydrocarbon materials in concentrations as low as 0.02%. Details of the procedure developed over the past eight year's use has been submitted for publication and should appear in the Anal. Ed. of the Ind. Eng. Chem. early in 1946.