from crude oils by two procedures: (1) the sample dispersed on kieselguhr is extracted with methyl nitrile in a Soxhlet extractor, and (2) the sample diluted with xylene is chromatographically adsorbed on silica gel and the complexes eluted with a polar solvent. Buncak (*14J*) stated the Czechoslovak specifications for fuel oils and described standard methods for determining various elements. Dwiggins *et al.* (*19J*) characterized chemical and physical properties of metalloporphyrin complexes by means of nuclear magnetic resonance, absorption spectrometry and small angle X-ray scattering. Studený (*67J*) described unrelated analytical procedures to determine several metals in used lubricating oils. Wiele and Kasten (*73J*) established a technique for the combustion and determination of inorganic substances containing sulfur and fluorine and of organic substances containing phosphorus, arsenic, vanadium, and lead by the Wickbold method using a metal burner.

Nonmetal Elements and Compounds

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Sulfur. Judging from the number of published papers, the main interest for sulfur analysts during the biennium has been improvements in methods for total sulfur determinations. Methods included combustion, reduction, X-ray analyses, and neutron activation.

Drushel (*33K*) used combustion of the sample followed by coulometric titration of sulfuric acid with sodium hydroxide. Chromniak and Jaworski (*24K*) burned the sample in a controlled oxygen atmosphere and titrated conductometrically with barium acetate; a back-titration of excess barium acetate with standardized sulfuric acid solution eliminated interference from other acids in the combustion products. A radiometric finish was used by Goode (*43K*) for microgram amounts of sulfur; barium chloride solution containing ^{133}Ba was used to precipitate barium sulfate in the combustion products, and the precipitate was washed with anhydrous methanol until constant activity was obtained. Trace amounts of sulfur were determined by Bychenkova and Shestakova (*20K*) by burning the sample in the air and converting sulfur to the sulfate, which was measured nephelometrically in an electric photocolorimeter; close agreement with the method of sulfur determination by Raney nickel reduction was obtained. Machida *et al.* (*77K*) measured small amounts of sulfur in heavy oils by burning the sample in an oxygen flask and measuring spectrophotometrically the complex formed with diphenylcarbazone. Total sulfur in fuels was determined by Ripperger (*103K*) by burning the sample at 750 °C in a quartz tube filled with quartz fragments and measuring the sulfur dioxide formed microcoulometrically; in a modification, individual sulfur compounds were determined by separating the sample on a GLC column before burning. Rebuzzini (*101K*) added ethylene glycol to improve the precision of sulfur determinations using the sodium peroxide bomb. Meador and Battles (*82K*) modified the aspirator–burner of the Hoggan–Battles combustion apparatus to eliminate vapor lock when burning light hydrocarbon samples. The Wickbold apparatus was modified by Wheatley and Barger (*139K*) to adapt the system to low sulfur (less than 50 ppm) samples and to high-boiling and shale oil fractions. Saori and Kanagawa (*104K*) reported good results for hydrotreated naphthas and kerosenes using Wickbold combustion with a chelatometric titration finish; sulfate in the combustion products is precipitated with excess barium chloride and the excess titrated with ethylenediaminetetraacetic acid. Dokladalova and Nekovarova (*30K*) reported an improved microcombustion technique which converts sulfur in organic samples to sulfur dioxide for spectrophotometric determination. The turbidimetric determination of sulfate without the use of additives was reported by Wimberley (*140K*); a barium sulfate dispersion was obtained by treatment with barium chloride dihydrate and the turbidity measured from the absorption at 480 nm. Combustion of the sample in an oxygen flask, followed by nephelometric determination of sulfate was recommended by Mendes-Bezerra and Uden (*83K*); techniques and reagents used permitted measurement of sulfate in the presence of excess barium.

Several methods for determining total sulfur by reduction were published. Gondermann (*42K*) determined total sulfur in volatile hydrocarbons by heating the sample with activated Raney nickel and measuring the resulting hydrogen sulfide by titration with mercuric acetate, or colorimetrically as methylene blue. Covic and Sateva (*26K*) diluted the sample with isooctane, reduced with Raney nickel and determined hydrogen sulfide by the titrimetric method of Granatelli. To determine sulfur in ethylene, Mamedova *et al.* (*80K*) reduced the sample with hydrogen over a platinum catalyst and measured the resulting hydrogen sulfide photocolorimetrically as methylene blue. Trace amounts of sulfur in hydrocarbons were determined by Farley and Winkler (*37K*) who pyrolyzed the sample, passing the products over platinum-on-quartz catalyst at 1200 °C; the hydrogen sulfide formed was converted to methylene blue by the addition of *N*,*N*-dimethylphenylenediamine and ferric ion and determined spectrophotometrically. Wallace *et al.* (*137K*) compared oxidative and reductive procedures, each with microcoulometric determination as the final step; interferences, precision, and limitations for each method are discussed.

A rapid method for sulfur analysis of crude oil and liquid hydrocarbon products by X-ray analysis, reported by Silipetar and Turina (*116K*), uses ^{55}Fe as the source. The determination of sulfur in heavy oils by vacuum-type fluorescence X-ray analysis was reported by Yanagase (*141K*); interferences from surface bubbles were reduced by using a lower temperature of measurement. In a later publication, Yanagase (*142K*) described the design of an apparatus to measure film rise and thickness, thus reducing uncertainties in measuring the sulfur content of heavy oils by fluorescence X-ray at reduced pressure. Novak and Veprek (*87K*) calibrated the interference effects of nitrogen, oxygen, vanadium, iron, and nickel when determining sulfur by radiometry using a ^{147}Pm/Al source. The use of a new device for rapid determination of sulfur in oil was reported by Inoue (*58K*) using a Pm/Al source. Continuous determination of the sulfur content of a mineral oil stream by measuring the amount of tritium radiation absorbed was reported by Trost (*134K*); density variations in the stream were compensated by measurements with the aid of gamma rays from ^{137}Cs.

Neutron activation was used by Elejalde and Albisu (*36K*) to determine sulfur and chlorine in petroleum products, and they suggest techniques to reduce interferences. Tamura (*130K*) studied the effects of interfering elements such as oxygen, nitrogen, silicon, and vanadium in the determination of sulfur in petroleum products by neutron activation.

Two papers described the separation and determination of sulfur compounds in petroleum gases by gas–liquid chromatography. Lulova *et al.* (*75K*) described a method for determining trace impurities of organosulfur compounds in petroleum refining gases, based on the combination of the equilibrium concentration method of organosulfur compounds with their subsequent gas-chromatographic separation and quantitative determination by β-ionization detector. Goode (*44K*) determined sulfur compounds in natural gas, taking advantage of their different retentions on different columns. Both papers report quantitative measurement of organosulfur compounds.

As little as 10^{-8} volume per cent of hydrogen sulfide in ethylene was quantitatively measured by Aivazov *et al.* (*2K*); H_2S from a 10-liter gas sample was sorbed on molecular seive, then desorbed by heating, and measured by GLC. Galanina and Kadarova (*41K*) determined H_2S in industrial gases by passing the sample through silver nitrate solution and comparing the intensity of the brown color formed with that of a standard. Hydrogen sulfide and thiols in gases were determined simultaneously by Drager (*31K*) using a silica gel column, the upper portion of which was impregnated with lead acetate and the lower portion with a mercury or copper salt; passing the sample through the column followed by a solution of sulfur in benzene caused measurable discoloration of the upper portion by hydrogen sulfide and of the lower portion by thiols. A polarographic method to determine hydrogen sulfide and elemental sulfur in petroleum was described by Obolentsev *et al.* (*92K*); the height of the polarographic peak was measured before and after bubbling nitrogen through the sample to remove hydrogen sulfide.

Sulfur present as thiols in crude oil was determined by Obolentsev *et al.* (*94K*) using amperometric and potentiometric titrations; both methods were found effective for low concentrations of thiols. Busev *et al.* (*19K*) determined thiols in catalytically cracked products by titrating with aqueous ethanolic 4-diethylaminophenylmercury acetate using diphenylcarbazone as the indicator. Podlipskii *et al.* (*98K*) recommended the determination of thiols in jet fuel by titration with aqueous silver nitrate–ammonia reagent and demonstrated with model compounds that aqueous copper sulfate–ammonia does not react quantitatively with secondary and tertiary thiols. Aronovich (*7K*) determined thiols in fuels with ammoniacal copper sulfate solution and a photoelectrocolorimeter; light permeability of the solution before and after addition of the sample was measured and the sulfur content calculated by two equations. Mixtures of primary, secondary, and tertiary thiols were separated by Leppin *et al.* (*73K*) using a GLC procedure; "functional retention indexes" of the different types were determined. Divalent sulfur compounds were determined by Holzapfel and Stottmeister (*55K*); an excess of a mercuric salt is added to the sample and the residual mercury measured by titrating with *S*-methylisothiouronium sulfate. Thiols and alkyl sulfides were separated from gasoline fractions by Obolentsev *et al.* (*93K*) using adsorption chromatography, with subsequent treatment of the concentrate with sodium-2-aminoethoxide in ethylenediamine to separate the thiols from the sulfides; several thiols and sulfides were identified by infrared spectra and mass spectrometry. Freedman (*40K*) analyzed mixtures of thiols and sulfides using a GLC technique with a capillary column coated with Triton X-100–Span 80. A GLC method for detecting and determining carbonyl sulfide in gases was described by Watanabe *et al.* (*138K*); water did not interfere.

Alkyl aryl sulfides were identified in crude oil by Hopkins *et al.* (*57K*), using a combination of infrared and mass spectra, GLC, and desulfurization. Numanov *et al.* (*89K*) extracted sulfides from a crude oil fraction with sulfuric acid and studied the extract by distillation, Raney nickel desulfurization of the fractions, and silica gel chromatography of the products. Numanov *et al.* (*88K*) used a mass spectrometric method to study the sulfides in a 150–350 °C fraction of a high-sulfur petroleum; the sulfides were classified as mainly thiacyclanes containing 1, 2, 3, and 4 rings, with monocyclics predominating. Khmel'nitskii *et al.* (*64K*) in a mass spectrometric study classified the sulfides in a 170–310 °C fraction of a crude oil; alkylthiacyclanes containing up to three rings were characterized; the sulfide concentrate, obtained by sulfuric acid extraction, contained 3.8 per cent thiophenes. The sulfides in a 170–310 °C petroleum fraction were extracted with sulfuric acid by Chertkov *et al.* (*23K*); the sulfides were further analyzed by re-extraction and adsorption chromatography on alumina, followed by iodometric and dielectrometric titrations and infrared spectroscopy. Yushko *et al.* (*143K*) analyzed the sulfur compounds in coke gas being used in the manufacture of ethylbenzene; thiols were oxidized to disulfides, and the sulfur compounds were then separated and analyzed by GLC.

Hopkins *et al.* (*56K*) identified 22 benzo[*b*]thiophenes in a crude oil distillate by a combination of chemical, chromatographic, and spectrometric methods. Oshima *et al.* (*97K*) oxidized the thiophenes in a petroleum aromatic fraction to obtain sulfones which were then separated chromatographically on silica gel; the sulfones were then reduced with lithium aluminum hydride to the original thiophenes which were determined by mass spectrometry. Uhdeova *et al.* (*135K*) used Raney nickel hydrogenolysis to determine benzothiophene in naphthalene; the benzothiophene was reduced to ethylbenzene which was then determined by GLC. Nigam *et al.* (*85K*), studying the hydrogenolysis of benzothiophene in naphthalene by Raney nickel, found the reaction was not quantitative, but that the end products—ethylbenzene and ethylcyclohexane—were proportional to the amount of benzothiophene and could be measured by GLC. Thiophenes in hydrocarbon mixtures were quantitatively reduced with Raney nickel by Staszewski *et al.* (*128K*); vapor-phase as well as liquid-phase reactions were studied, and the method was deemed feasible for reaction gas chromatographic analyses.

Characterization and determination of the sulfur compound types in petroleum and petroleum fractions were the objects of several investigations. Drushel (*35K*) determined sulfur compound types using in-line catalytic or noncatalytic pyrolysis, followed by gas-liquid chromatography with microcoulometric detection; the analysis time was 1 hour with a precision of 2 or 3% for the various types. Sevast'yanova and Ivchenko (*112K*) compared the composition of groups of sulfur compounds in the 28–350 °C fractions from two crude oils; the groups were obtained by fractional elution with different solvents from a silica gel column. Thiols and disulfides (after reduction) were determined in commercial gasolines by Gulyaeva and Blokh (*48K*) by potentiometric titration of the samples with ammoniacal silver nitrate solutions; sulfides were determined by direct titration with potassium iodate. Brodskii *et al.* (*15K, 16K*) developed a mass spectrometric method for analyzing sulfur compound concentrates isolated from medium-boiling-range petroleum fractions; the authors used synthetic mixtures of aliphatic, cyclic, and cycloalkyl sulfides; thiophene derivatives; and both saturated and aromatic hydrocarbons to determine mass numbers of characteristic ions, characteristic sum numbers, and sensitivity coefficients. The types of sulfur compounds in high-boiling fractions of Middle East and Venezuelan crude oils were studied by Bestougeff and Joly (*13K*); infrared, ultraviolet, mass and NMR spectrometry, GLC and potentiometric titration were employed in the analysis of fractions separated by adsorption chromatography. Organosulfur compounds in gasoline were identified by Obolentsev *et al.* (*91K*), using GLC and reaction GLC; retention indexes of cyclic and aliphatic sulfides, thiophenes, and disulfides were tabulated. Snegotskii and Snegotskaya (*118K*) studied the feasibility of using thin-layer chromatography to differentiate, separate, and identify the sulfur compounds in petroleum products; solvents for differentiation of various groups of compounds on alumina were recommended. Ahmed *et al.* (*1K*) carried out a detailed analysis to obtain the quantitative distribution of sulfur compound types (also elemental sulfur) in petroleum distillate fractions boiling up to 350 °C. Schulthiesz *et al.* (*105K*) described a method to analyze the sulfur compounds in cracked gasolines; a concentrate prepared by liquid chromatography was analyzed by GLC and mass spectrometry. Ratovskaya *et al.* (*100K*) studied the distribution of sulfur in kerosene and distillate fuels using polarography and titrimetry.

A critical review of methods for determining elemental sulfur, hydrogen sulfide, and the various types of sulfur compounds occurring naturally in petroleum or formed during processing was made by Drushel (*34K*); included is a summary of data on sulfur compounds identified and a comprehensive bibliography.

The distribution and group analysis of sulfur compounds in crude oils of the USSR and in the gasoline and kerosene distillates from these crudes were studied by Obolentsev (*90K*), who related the thermal stability of the compounds, and the amounts of thiols and elemental sulfur in the crude oil, to the nature of the reservoir rocks; a method for separating thiols from kerosene distillates and suggested commercial uses of the thiols were presented.

Nitrogen. The petroleum industry has been especially active in the past two years in investigating the nitrogen compounds present in high-boiling distillates. This information is needed by the industry because of the desire to convert this material to clean fuel.

A comprehensive study was made by Snyder *et al.* (*124K*, *120K*, *121K*) of the nitrogen and oxygen compound types present in the 400–700°, 700–850°, and 850–1000°F distillates of a California petroleum, respectively. Major nitrogen compound types found in all three distillates included indoles, carbazoles, pyridines, quinolines, pyridones, and quinolones. The higher-boiling distillates contained benzologs of these types. Nitrogen and oxygen compounds comprise 3 weight per cent of the lower-boiling distillate, 13 weight per cent of the middle distillate, and 21 weight per cent of the higher-boiling distillate. In his American Chemical Society Petroleum Chemistry award address, Snyder (*119K*) discussed the structural patterns of nitrogen and oxygen compounds in the 400–1300 °F distillates. A critical evaluation of rapid methods for routine analysis of petroleum fractions for nitrogen and oxygen compound types was also presented.

Investigation of the basic nitrogen compounds in the 250–300 °C fraction of Wilmington (Calif.) petroleum by Brandenburg and Latham (*14K*) resulted in the identification of an alkyl-substituted cyclopentapyrindan and an alkyl–cycloalkyl-substituted pyridine; the cyclopentapyrindan was the first compound of this type identified in petroleum. Nishishita *et al.* (*86K*) made a mass spectral analysis of the nitrogen compounds in a 290–310 °C distillate of Kuwait petroleum; the $C_nH_{2n-5}N$ (pyridine) series was the most abundant; the carbon number distribution examined was between C_{10} and C_{21} with the apex located from C_{13} to C_{16}. Basic and neutral nitrogen compounds in heavy-end fractions of Baku crude oil were investigated by Madkour *et al.* (*78K*, *79K*); the bases were characterized as primary, secondary, and tertiary amines, using potentiometric titration; the neutral nitrogen compounds were probably bicyclic *N*-substituted carboxylic amides as shown by functional and spectrometric analysis. Tokareva *et al.* (*133K*) reported the distribution of total and basic nitrogen among asphaltenes, resins, and oils of Mangyashlak crude oils. The nitrogen compounds in an acid extract of Dzharkurgan petroleum were examined by Speshilova *et al.* (*125K*); the authors reported 31.8% tricyclic bases, 28.7% monocyclic bases, and 39.5% bicyclic neutral compounds present in the extract. Kiricenkova *et al.* (*65K*) investigated the distribution of nitrogen compound types in distillates from Romashkino-Mukhanov crude oil by potentiometric titration and infrared spectrometry. The direct proportionality between the content of nontitratable nitrogen and the absorptivity of the N-H infrared band permitted the direct determination of nontitratable nitrogen by infrared spectrometry.

The nitrogen bases in a shale oil naphtha were separated and identified by Brown *et al.* (*17K*), who identified 50 individual compounds by mass, infrared, and NMR spectral analysis; about 64% of the bases are alkyl-substituted pyridines, 33% alkyl-substituted anilines, and the remaining 3% a mixture of quinolines and cycloalkanopyridines. Koros *et al.* (*68K*) investigated the nitrogen compound types present in shale oil and followed the changes in these types during hydrodenitrogenation of the oil using potentiometric titration, infrared analysis, and Kjeldahl nitrogen determination; the distribution of aliphatic and aromatic amines, and of 5- and 6-membered-ring nitrogen compounds is presented for samples before and after hydrotreating.

Several researchers developed separation methods for nitrogen compounds. Snyder and Buell (*123K*) utilized cation- and anion-exchange resins in conjunction with adsorption chromatography on alumina, silica gel, and charcoal in an integrated separation scheme for nitrogen and oxygen compound types in high-boiling fractions. The fractions obtained were analyzed by high-resolution mass, infrared, ultraviolet, and NMR spectrometry. Jewell and Snyder (*60K*) reported the selective separation of "non-basic" nitrogen compounds from petroleum distillates by forming coordination complexes with ferric chloride supported on kaolin; the nitrogen compounds are recovered by eluting the complexes with 1,2-dichloroethane, passing the eluate through an anion-exchange resin, which decomposes the complex and retains the metal salt.

Nitrogen compounds were separated from distillate fractions of petroleum and shale oil using chemical treatment, thermal diffusion, and liquid–solid and gas–liquid chromatography according to a paper by Haines *et al.* (*51K*); the nitrogen was characterized by types, using a potentiometric titration method.

A rapid liquid–solid chromatographic procedure for the routine qualitative and quantitative analysis of hydrogenated quinoline mixtures was developed by Snyder (*122K*); the method involves solvent program elution of the sample from a column of F-20 alumina partially deactivated with water. Barsch *et al.* (*9K*) used thin-layer chromatography to separate a mixture of alkyl-substituted pyridines. The degree of adsorption was found to decrease with increased alkyl-chain length.

A method for determining nitrogen compound types by a combination of pyrolysis, gas chromatography, and microcoulometry was reported by Drushel (*32K*); the basic nitrogen compounds are extracted with acid and run separately to minimize elution overlap. Oita (*95K*) described an inlet system that permits the introduction of viscous or solid samples into a commercial coulometric analyzer without exposure to the atmosphere. Microcoulometry was used by Drushel (*33K*) in the determination of nitrogen, sulfur, and chlorine in petroleum and shale oil fractions; nitrogen analysis involves hydrogenolysis on granular nickel and coulometric determination of the resulting ammonium ions.

Gas–liquid chromatography (GLC) was used by several researchers to separate nitrogen compounds. Karayannis *et al.* (*63K*) developed a high-pressure gas chromatograph and investigated several column packings for their ability to resolve porphyrins. Poulson (*99K*) studied three stationary phases for the separation of basic and nonbasic nitrogen compounds by GLC. Retention data and bleed rates for Triton-S-305, Carbowax 20M, and Carbowax 20M-TPA were reported. Kaluza and Martin (*62K*) investigated the GLC behavior of several alkyl-substituted pyrroles and found that these thermolabile compounds did not isomerize at 190 °C. A GLC detector using a hydrogen–air flame with a burner jet constructed of rubidium sulfate was described by Hartmann (*52K*). This alkali flame detector was reported to give a selectivity of 1000 to 1 for organic nitrogen compounds over hydrocarbons.

An automated method for determining trace quantities (0–200 ppm) of nitrogen in petroleum distillates was reported by Heistand (*53K*) using a unique sulfuric acid extraction coil followed by continuous Kjeldahl digestion and colorimetric indophenol blue detection of the ammonium ion. Smith *et al.* (*117K*) modified the extractive percolation method by converting the ammonium ion into indophenol blue and measuring the extinction at 625 nm. Samples containing as little as 50 μg of nitrogen can be analyzed with this technique. Gouverneur and Van de Craats (*47K*) compared the extractive percolation, oxyhydrogen combustion, and hydrogenation–coulometric methods for determining nitrogen in trace amounts.

Two patents were issued to Shell Internationale Research Maatschappij N. V. (*114K*, *115K*) describing the determination of nitrogen by burning the sample in an oxy-hydrogen flame. The method involves oxidizing the nitrogen oxide with ozone, potassium permanganate, or chromous carbonate to nitrogen dioxide which is absorbed in aqueous isopropyl alcohol and measured by electrical conductivity. Wickbold oxyhydrogen combustion was used by Gouverneur *et al.* (*46D*) to determine nitrogen in oils. The nitrogen oxides are adsorbed on sodium chloride supported on alumina, reduced to ammonia with Devarda's alloy, and titrated with hydrochloric acid.

Caughley and Joblin (*21K*) developed a high-frequency titrimetric method for determining "total base number" of lubricating oils. This method is reported superior to the ASTM D664 method in that electrode contamination is eliminated, analysis time is shortened, and sharp end points are obtained without the use of a buffer. Vaughn and Swithenbank (*136K*) investigated the technique of enthalpimetric titration of basic nitrogen compounds. Weak and strong bases were differentiated by titration in acetone and acetic acid solvents. Results obtained using this method on several tar products were found comparable to those obtained by potentiometric titration. The precipitation titration of nitrogen bases using biamperometric end-point indication was studied by Ashworth and Hartmann (*8K*); the effects of several experimental parameters were observed during the titration of model basic nitrogen compounds with 0.1M iodine in acid solution. A spot test for pyridine derivatives was reported by Larue (*71K*) who used trisodium pentacyanoamminoferrate to form a colored complex.

A neutron activation method for determining nitrogen in petroleum distillates was developed by Tamura (*131K*). The method is applicable to samples containing more than 0.1% nitrogen. The weight per cent of organic carbon in the sample must be known to obtain satisfactory results.

A modified Kjeldahl method by Stankevich and Borisova (*126K*) for the determination of nitrogen in light distillates used acid extraction for samples containing small amounts of aromatics and extractive percolation through a column of acid supported on pumice for samples containing large amounts of aromatics.

Thompson *et al.* (*132K*) developed a microhydrogenation technique for use in nitrogen compound identification studies. The nitrogen atom is removed by vapor-phase catalytic hydrogenation, leaving a hydrocarbon with a structure that can be related to the original nitrogen compound.

Oxygen. The determination of total and dissolved oxygen received less attention than in previous years. Total oxygen was determined by Gouverneur and Bruijn (*45K*) using a modified Schütze–Unterzaucher carbon reduction micromethod including a manometric carbon dioxide finish. Ishii (*59K*) measured dissolved oxygen in gasoline by alternating current polarography using ethanolic sodium hydroxide as the supporting electrolyte. Ford (*39K*) separated the dissolved oxygen in hydrocarbon streams by gas chromatography on a squalane–Celite column followed by a molecular sieve column and determined the oxygen with an electron capture detector. Guyot and Vialle (*49K*) determined 1 ppm or less of dissolved oxygen and water by reacting the sample with an organometallic compound such as butyllithium; water reacts to produce the hydrocarbon which is separated and analyzed by GLC; oxygen reacts to produce an alkoxide, and the oxygen content is calculated from the difference between the amount of organometallic compound added and the amount consumed by the sample.

Water in gases was the subject of six papers. The water content of a butane–butylene fraction was measured by Berezkin *et al.* (*11K*), using GLC with polyethyleneglycol–Sferokhrom-1 columns Leonhardt (*72K*) determined water in town gas using a β-ionization detector after separation on a GLC column of Porapak Q or of PTFE plus polyoxyethylene glycol. A nomograph for finding the water content of natural gas under various conditions (−60 to +70 °F and 14.7 to 1000 psi) was published by Davis (*28K*). Anthony and McKetta (*5K*) used a correlation to estimate the mole fraction of water in hydrocarbon-rich vapor in the two-phase region—hydrocarbon-rich vapor and water-rich liquid. A correlation procedure for predicting water content of natural gas by Sharma and Campbell (*113K*) depends upon basic fugacity concepts and the McLeod and Campbell method for predicting critical conditions.

Modifications of the Karl Fischer method for the determination of water continued to appear. Klimova *et al.* (*66K*) suggested an electrometric method in which dimethylformamide was substituted for methanol in the reagent. L'vov *et al.* (*76K*) hermetically sealed the apparatus to eliminate atmospheric moisture and used a combination of two burets containing Karl Fischer reagent with different titers. Covic-Horvat and Sateva (*27K*) used *N*-ethylpiperidine as a catalyst in the determination of 5 to 100 ppm of water in liquid hydrocarbons.

Water in petroleum products was determined by Orzherovskii (*96K*) using a thermochemical method which depends on the heat of reaction with calcium hydride. Lizogub and Esel'son (*74K*) used a special infrared spectrophotometer with glass optics and measured absorption at 1.37–1.87 μm. Methanol was used as an internal standard in a gas chromatographic method by Hogan *et al.* (*54K*) which used Porapak Q as column packing.

Acid numbers of petroleum products were determined by Filenko *et al.* (*38K*) by potentiometric titration with tetraethylammonium hydroxide in ethanol using glass and calomel electrodes; other electrodes and titrants were also studied. For the titration of weak and very weak acids, Nakajima *et al.* (*84K*) suggest potentiometric titration with tetramethylammonium hydroxide in pyridine. Berezkin *et al.* (*12K*) determined the acid impurities in gases (*e.g.*, carbon dioxide and hydrogen sulfide) by absorbing the acids in potassium hydroxide solution then adding acid to liberate the gases into a GLC column for analysis.

In a study of the interfacially active acids, Seifert and Howells (*107K*) extracted a California crude oil with alcoholic sodium hydroxide to obtain an acid fraction. This fraction was treated by a sequence of exhaustive back extractions, ion-exchange, and silica gel chromatography to separate the carboxylic acids from the phenols. The carboxylic acids were found to be the interfacially active component. Seifert and Teeter (*108K*) subjected these carboxylic acids to preparative thin-layer chromatography followed by high-resolution mass spectrometric studies of the acids and of their trihydroperfluoroheptyl esters to indicate the presence of classes falling in the $Z = +2$ to $Z = -26$ mass spectral series. In a further study, Seifert *et al.* (*111K*) identified many classes of carboxylic acids by converting the acids, through the alcohols and *p*-toluenesulfonate esters, to hydrocarbons which were separated and identified. Seifert and Teeter (*109K*) applied combinations of NMR, high-resolution mass, ultraviolet, fluorescence, and infrared spectrometry and GLC to these hydrocarbons to elucidate many structural features of substituted naphthenic, naphtheno-aromatic, and mono- and diaromatic carboxylic acids. Extension of the investigations by these authors (*110K*) revealed many classes of heteroatomic carboxylic acids. These studies show that the "naphthenic acids," which traditionally have been considered to be primarily mononaphthenic and alkanoic acids, include a wide variety of compound classes.

In a study of the acids in the diesel oil fraction of Chernuskin crude, Kozlov *et al.* (*69K*) converted the acids to sodium salts and treated them repeatedly with aqueous calcium hydroxide until reproducible refractive index values were obtained. The regenerated fractions were studied by infrared spectra, acid number, molecular weight, boiling point, elemental composition, and surface tension. These data plus *ndm* data on hydrocarbons derived from the acids and the results of dehydrogenation of these hydrocarbons showed that the aliphatic acids had branched chains and the naphthenic acids contained a single cyclopentane ring. Anbrokh *et al.* (*4K*) separated the normal alkyl acids from a refinery alkali extract using urea and found that these fatty acids made up 20% of the acid mixture; the acids were identified by GLC of their methyl esters.

Dicarboxylic acids obtained during oxidation of kukersite kerogen were converted to dimethyl esters and analyzed gas chromatographically by Mannik *et al.* (*81K*). Richter *et al.* (*102K*) reported the detection and identification of oxocarboxylic and dicarboxylic acids in complex mixtures such as oxidized Green River formation kerogen using reductive silylation and computer-aided high-resolution mass spectral data.

The acids that act as natural emulsion stabilizers in crude oil were separated and analyzed by Stout and Nicksic (*129K*) using gel permeation and ion-exchange chromatography. Akhundova *et al.* (*3K*) used the Bjerrum procedure to measure the dissociation constants of the naphthenic acids recovered from oil well water. Starkova and Svest'yanova (*127K*) published a rapid method for determining the concentrations of naphthenic acid salts in which the sample is dissolved in an alcohol–glycerol mixture and titrated with hydrochloric acid.

Phenols were the subject of several papers. Diamond (*29K*) suggests the analysis of normal C_1 to C_{12} *p*-alkylphenols in lubricating oils by thin-layer chromatography of a chloroform solution on polyamide with sodium hydroxide–methanol as solvent and detection with Fast blue salt B. Traces of phenols in water or acetone were determined by Cohen *et al.* (*25K*) by reacting the solutions of phenols with 1-fluoro-2,4-dinitrobenzene and GLC (with electron capture detection) of the resulting 2,4-dinitrophenyl ethers. Argauer (*6K*) reacted sodium hydroxide solutions containing as little as 0.01 ppm of phenols with chloroacetic anhydride in benzene and separated the resulting chloroacetate derivatives by GLC with electron capture detection. Seifert (*106K*) studied the effect of phenols on the interfacial activity of crude oil by progressive esterification of the carboxylic acids under conditions that left the phenols unmethylated.

Selective detection of oxygen compounds in GLC effluents was achieved by Kojima *et al.* (*67K*); the column effluent is passed over platinum–carbon at 900 °C to convert the oxygen to carbon monoxide, and then, after removing interfering gases, over iodic acid at 120 °C to convert the carbon monoxide to carbon dioxide. After removal of iodine, the carrier gas and carbon dioxide are passed into a stream of water which is monitored by an electrical conductivity cell.

An integrated scheme for the separation of the oxygen and nitrogen compounds in high-boiling petroleum distillates was developed by Snyder and Buell (*123K*). The scheme involves ion-exchange and adsorption chromatography on alumina, silica, and charcoal. Using this scheme to prepare fractions which were examined by high-resolution mass spectrometry and other techniques, Snyder has examined 400–700 °F (*120K*), 700–850 °F (*124K*), and 850–1000 °F (*121K*) distillates of a California petroleum. Major oxygen compound types found included pyridones, dibenzofurans, dihydrobenzofurans, phenols, and their benzologs and aliphatic esters and ketones, sulfoxides, and carboxylic acids. Snyder (*119K*) summarized these investigations in an ACS Petroleum Chemistry Award address.

Two methods for characterizing oxygen compounds depend on hydrogenation. Thompson *et al.* (*132K*) developed a microhydrogenation technique which removes the oxygen atom without disturbing the carbon structure; identifications of the resulting hydrocarbons are thus helpful in characterizing the parent oxygen compound. A microreactor gas chromatographic method for identifying oxygen compounds of linear structure published by Krasnoshchekova and Klesment (*70K*) depends upon the hydrogenation of the sample with a platinum or palladium catalyst on molecular sieve; the adsorption of the straight-chain hydrocarbons on the molecular sieve and their disappearance from the chromatogram permits distinction of linear from cyclic or branched chains.

Samples produced by liquid-phase oxidation of *n*-paraffin fractions were analyzed by Brown *et al.* (*18K*) by separation on silica gel followed by potentiometric titration, gas chromatography, and mass and infrared spectrometry. Chamberlain (*22K*) made detailed correlations of the nuclear magnetic resonance chemical shifts of oxygenated unsaturated aliphatics. Bartonickova (*10K*) analyzed the neutral oils from the refining of phenol–cresols by petroleum naphtha by comparing the gas chromatographic behavior on columns of Apiezon and PEG 400 supported on Chromosorb.

Halogens. The halogen content of highly halogenated organic compounds was determined by Habashy *et al.* (*50K*) using polarography after combustion in an oxygen flask. Kainz and Wachberger (*61K*) determined traces of chlorine in crude oil by combustion followed by nonaqueous potentiometric titration. Neutron activation analysis was used by Elejalde and Albisu (*36K*) to determine sulfur and chlorine in petroleum products. Drushel (*33K*) suggests determination of chlorine by combustion followed by microcoulometric titration.

Analytical and Process Instrumentation

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The applications and uses of automatic process analyzers in refineries continue to be emphasized in the technical literature more than the development of new analyzers. This emphasis on pragmatism over research reflects something of a sense of frustration because achieving optimization of process operations has, in too many cases, fallen short of expectations. Analysis instrumentation lies at the heart of complex control schemes; much attention is therefore being given to making analyzers operate more dependably and to assure that they are installed in the right place and manner. Also, the continuing emphasis on practices is both symptom and partial cause of the more significant trend of control theory and technology to outstrip measurement technology. In the nature of things, this imbalance will eventually be righted.

In this connection, the January 1970 issue of *Instrumentation Technology* heralding the 25th anniversary of the Instrument Society of America is most interesting. Staff articles (*32L*) that review achievements since 1945 and identify unfilled needs list the development of on-stream analyzers among the