Gas Analysis

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This review represents the author's choice of the important contributions to gas analysis since the last review (September 1961 through September 1963). The author has followed the general pattern of previous reviews. This is rather selective because of the large volume of contributions to gas analysis and it is hoped that most of the important and informative items have been selected for the reader's use.

NITROGEN AND NITROGEN COMPOUNDS

Two methods are described by Sychev and Sycheva (193) for the rapid analysis of nitrogen-argon mixtures: spectrography and measurement of the ignition potential of the glow discharge. In spectrographic analysis the spectra are excited in a hollow cathode. The analysis is made from the edge of the nitrogen band at 4709A, and the line argon 4736A. The second method is based on the increase in the ignition potential of the glow discharge as the content of nitrogen in argon increases. The process is carried out at a current strength of 50 ma, and 1 mm.: the potential of the discharge is measured with a voltmeter. Fay, Mohr, and Cook (57) use a high voltage silent electrical discharge tube to excite argon-nitrogen mixtures to photoemissive energy levels. The tube operates at atmospheric or higher pressures on continuous flow samples.

An automatic gas analyzer for determining small amounts of nitrogen in argon is based by Aleksandrov and Borok (3) on the comparison of the intensity of two light beams, one of which is characterized by nitrogen lines and the other argon lines. Particular attention is given to the dimensions of the discharge tube used for the high frequency electrodeless discharge which is used in the analyzer.

In the presence of dienes, Bokhoven and Tomassen (19) have shown that trace quantities of nitric oxide in coke oven gas can be oxidized to nitrogen dioxide by irradiation with a high-pressure mercury vapor lamp. A continuous nitric oxide recorder is described based on the above reaction and the subsequent absorption and reaction with the Griess-Ilosvay reagent. The method is also applicable to air-pollution analysis. Hummel and Kaltenhaeuser (93) have used the fact that nitric oxide forms a stable colored complex in solution, with ferrous thioglycolate, thiosul-

fate, or cysteinate. Nitric oxide is determined in a gas containing unsaturated hydrocarbons by mixing a known amount of the flowing gas with a known amount of the flowing reagent, separating the solution and passsing it through a colorimeter.

Nitrogen dioxide is measured by Borok (20) by using the principle of measuring the change of the electrical resistance of a heated current-carrying conductor located in a gas mass, some components of which are subject to thermal dissociation. The change of the conductor's electrical resistance is proportional to its temperature change, and accordingly to the concentration of the dissociated component.

A coulometric method is used by Rostenbach and Kling (159) for the detection of nitrogen dioxide. air sample enters an annular space in intimate contact with a potassium bromide solution flowing over a platinum electrode. A d.c. potential supplied by a mercury battery is applied to the electrodes. In the presence of nitrogen dioxide, bromine is released and the flow of current is indicated on a microammeter. Heinrich and Draeger (86) give a detector for nitrogen dioxide which is made from a glass tube filled with granular carrier of benzidine derivatives and from the length of the colored zone and the volume of gas, the amount of nitrogen dioxide in the gas is determined. Kinosian and Hubbard (109) give a simple, rapid, and convenient semiquantitative method for determining nitrogen dioxide in air. The method does not appear to be susceptible to interference from nitric oxide or other gases commonly found in industry.

An apparatus for rapid routine determination of nitrogen oxides in the atmosphere is given by Gidaspov (67). The apparatus consists of a container for glass ampoules containing silica gel impregnated with Griess reagent, a screw clamp for crushing the ampoules, and a reaction chamber in which the silica gel changes its color upon exposure to the atmosphere. To determine the concentration of nitrogen oxides, the color is compared with a corresponding color of a control scale, placed in the reaction chamber.

Skorodumov (172) states that for a more accurate determination of the total concentration of nitrogen oxides in the air, the amount of anions of nitric and nitrous acid should be determined simultaneously in the absorbent liquid. A 1-hour contact of the

gas-air mixture and the absorbent liquid in the gas pipet is sufficient for complete absorption of nitrogen oxides from the air sample.

Nitrogen oxides in flue gases are determined by Leithe (127) by shaking the sample with hydrogen peroxide containing a foaming agent. Absorption is complete in five minutes. The resulting nitric acid is titrated with standard caustic by using a methyl redmethylene blue mixed indicator.

Continuous recording of the nitrogen oxides in a gas stream is accomplished by Schuff et al. (168) by adding at least 600% hydrogen and passing the mixture over copper metal in wire form at 450° C. to reduce the oxides to ammonia. This is then absorbed in sulfuric acid and the electrical conductance of this solution determined before and after absorption of the treated gas stream.

Tada (194) evaluates the standard colorimetric methods of nitrite and nitrate determination. Supplemented by techniques for oxidation of nitric oxide to nitrite or nitrate, these form the basis of a proposed procedural scheme for the analysis of the different oxides of nitrogen in air.

The reaction between hydrogen cyanide and copper acetate is used by Lu (132) for the automatic determination of hydrogen cyanide. The reaction produces active oxygen which reacts in turn with 2,3'-dimethylbenzidine to produce a yellow color, which is measured by an automatic recording colorimeter. Tanaka and Yamamoto (197) have determined hydrogen cyanide by the reaction of mercuric diphenylcar-bazide paper.

Acrylonitrile (199) reacts with hexamethyleneimine in the presence of ACOH to form β -(N,N'-hexamethyleneamino)propionitrile which is titrated with standard hydrochloric acid in methanol using a mixture of methylene blue-methyl red as indicator.

Nitrogen trichloride in liquid chlorine may be determined by converting the nitrogen trichloride to ammonium chloride followed by determining the ammonia by the indophenol. De Vries, Savariar, and Chakrabartty (45) report the conversion by evaporation of the chlorine through hydrochloric acid.

Bukina (29, 30) gives methods of determining nitrosyl chloride iodometrically with other oxidants absent and determination of nitrosyl chloride in the presence of chlorine and hydrogen chloride.

It has not been very many years since the Hersch cell for the analysis of oxygen in gas streams became popular. This has been the starting point for many modifications. Mancy, Okum, and Reilley (136) have used a silver electrode in the place of the platinum. A thin polyethylene membrane is fixed in close contact with the electrode surface so that oxygen can diffuse rapidly to the electrode surface. Kinsey (110) has patented a cell consisting of a silver cathode enclosing a sheath of porous polyvinyl chloride, inside which is an anode of metallic tantalum. electrolyte is an aqueous solution of tantalum hydroxide or the double carbonate of tantalum. Borok and Alitovskii (21) have used a thermostatic electrochemical cell consisting of a lead anode separated from a silver grid cathode by a porous glass membrane. A Belgium patent (13) describes a cell with three electrodes e.g., a silver cathode with a diffusion screen for admitting the test gas, a platinum anode, and a lead anode. These are connected to a battery and a transistor in such a way that the main current flowing between the platinum and the silver is controlled by the current between the lead and the silver. main current is measured by a milliammeter and is calibrated against gases with known oxygen content. A German patent by Toedt (205) is for a galvanic cell for determination of oxygen.

A cell consisting of copper/aluminum/solution/potassium chloride/agar bridge/saturated calomel electrode/copper has been used by Scarano (164–166) to determine traces of oxygen. A specially treated 99.99% pure aluminum electrode is used.

Borok and Mironov (22) have developed a device consisting of a continuous galvanic oxygen analyzer and an enriching glass column filled with silica gel and placed in liquid nitrogen. The sensitivity threshold is 2×10^{-5} ml. of oxygen.

A simple cell, Cd(CrCl2)C, for determination of oxygen was studied by Buchur (28) in which electrolyte is obtained directly by chemical reduction. A potential appears instantaneously on the carbon electrode in the presence of oxygen, its value being determined by the partial pressure of oxygen. A series of oxidation-reduction reactions causes a current to appear in the external circuit, the value of which depends on the quantity of oxygen absorbed. The reactions, the apparatus, and the mode of operation are described. Teske (202) describes an automatic electrochemical oxygen analyzer which is used to determine parts per million of oxygen by amperometric titration. The oxygen-containing gas, dried by passing through silica gel, is led by a steel tube

into the electrolyte container and circulated. The electrolyte solution is mixed rapidly by magnetic stirrer, reaching equilibrium with the oxygen. A silver wire indicator electrode and lead anode are used.

A method and apparatus for determining oxygen, based on the so-called concentration chain principle, are given in a German patent by Spracklen, Campbell, and Fellows (180). The rotary and stationary electrodes consist of carbon, glass, or plastic. An ammoniacal ammonium chloride solution containing copper is a useful electrolyte, regenerated by using metallic copper.

An instrument is described by Greenspan (73) to monitor partial pressure of oxygen based on the critical flow pneumatic bridge analogous to a Wheatstone bridge where orifice or nozzle elements are the analogs of resistance elements and a differential pressure gage replaced the galvanometer. A special absorber, cobalt oxide, is incorporated into one branch of a balanced bridge, and pressure unbalance, approximately proportional to the partial pressure of the absorbed gas, is measured.

The use of thermomagnetic principles for oxygen determination is given by Ageikin (2), Knipping (115), Engelhardt (55), and Kichigin (106). Comparison of absorbing reagents for oxygen is given by Kavan and Jaromir (105). Skripka and Dykhno (173) use the photocolorimeter after absorbing the oxygen in a solution containing cuprous chloride, ammonium chloride, and ammonium hydroxide. Feder and Craft (58) suggest the combining of the oxygen with hydrogen and using an electrolytic moisture analyzer for determining the moisture produced. By measuring the resistance of a cuprous oxide wire at 1050° C., Duquesnoy and Marion (49) determine the amount of oxygen present in a noncombustible gas.

A self-sampling indicator tube for oxygen consists of a sealed evacuated tube filled with a silica gel-manganous oxide mixture prepared in situ. Dixon and Kiff (46) state that when air is admitted by breaking the end of the tube, the oxygen content is determined from the lengths of changed (brown) and unchanged (green) material. A batch calibration curve is necessary.

Nief and Severin (148) give a prior treatment of the ion source of a mass spectrometer so that analysis of trace oxygen in carbon dioxide are possible with the mass spectrometer.

One of the common methods of determining dissolved oxygen in water is by the polarograph. Briggs and Knowle (26), Samsoni (162), Longmuir and Allen (131), Heimann and Wisser (80), and Barbi (9) give modifications of the polarograph procedure to improve the determination and reduce the effects of interference. Stracke (187), Crocker

and Williams (40), and Smit and Ehrenburg (174) have modified the Winkler method of dissolved oxygen analysis so that they obtain results for lower concentrations and reduce errors in the method. Toedt (204) discusses the automatic amperometric titration of oxygen by using an electrochemical dissolved oxygen recording apparatus. Hissel and Pire (89) have used coulometry at constant current for the microdetermination of dissolved oxygen in boiler-feed water. The phase-exchange (7) process is a continuous method of measuring oxygen dissolved in water and is independent of impurities contained in the water.

An electrolytic moisture detector is used by Bentley and Cole (16) for oxygen detector and determination. The oxygen is freed from the water and dried and then treated with hydrogen to form water which is measured by the electrolytic moisture detector.

Electron skin resonance spectroscopy is utilized by Ingalls and Pearson (96) for the determination of dissolved oxygen. Indigo carmine is oxidized by dissolved oxygen in water. The change in color of the dye is directly proportional to the amount of dissolved oxygen. Santoro and Powell (163) use a Johnson color comparator to determine the dissolved oxygen content of water.

Imai, Chaki, and Tanaka (95) have devised an apparatus in which dissolved oxygen is expelled by a stream of nitrogen and made to react with powdered copper. Ammonium hydroxide is passed through the column of powdered copper and the cuprous oxide formed by the expelled oxygen is converted to Cu- $(NH_3)_4$ ⁺. This is oxidized with hydrogen peroxide and the absorbance read at 585 m μ .

Kapff and Jacobs (103) have constructed a chamber where the liquid and the dissolved gas are brought into equilibrium. A constant liquid level is maintained at the bottom of the chamber. At the top of the chamber there is a vent which exhausts to the atmosphere, through which oxygen or air can flow freely in or out. A detector capable of determining the direction and rate of flow of the gases is placed in the vent. The direction of flow depends on whether the liquid is unsaturated or supersaturated.

SULFUR COMPOUNDS

Romovacek, Simanek, and Nedomlel (158) describe a method for the determination of total sulfur in highly volatile fluids. The material is injected by means of a simple device into a polyamide or polyethylene capsule which is hermetically sealed, inserted into a colorimeter, pressured to 30 atmospheres with oxygen, and exploded.

The nitrogen dioxide and sulfur trioxide are absorbed in hydrogen peroxide, and sulfate is determined by complexometric titration with barium chloride with Eriochrome Black T as indicator or by indirect conductometric titration.

Gaseous or liquid hydrocarbons are burned in an oxyhydrogen flame, the products conducted over heated quartz beads to ensure complete combustion of the sulfur compounds, and the combustion products absorbed in hydrogen peroxide. The sulfate in the reduced volume of absorbent is determined by using mixed thorin-methylene blue indicator. Hoggan and Battles (91) give that this method is useful for sulfur concentrations up to 400 p.p.m.

A British patent (27) describes a method and apparatus for continuously determining the sulfur in a gas stream by means of x-ray absorption from an Fe⁵⁵ source. Other elements do not interfere.

Kobayashi (116) has prepared detector tubes for the rapid microdetection of sulfur dioxide in air. The detector reagent consists of purified silica gel impregnated with iodine solution and bis (p-dimethylaminophenyl) methane. Quantitative estimation is made from the length of the colored portion of the column.

Cloth saturated with lead dioxide is used by Wyszynska and Kosinski (215) to determine sulfur dioxide in air. Ioanid et al. (97) suggest that the air be passed through a dilute solution of potassium dichromate containing a small quantity of potassium iodate and starch as indicator. When the entire quantity of bichromate as well as that of liberated iodine is consumed, the blue coloration disappears, indicating the end of the reaction.

Makrinov (135) states that stringent control of air velocity and total volume of air passed through a standard starch iodine solution is necessary to give good results.

Terraglio (201) has evaluated the spectrophotometric method, iodimetric method, and an acidimetric method for the determination of sulfur dioxide. The acidimetric and spectrophotometric methods gave comparable average recoveries while the iodimetric method recoveries were lower. Ozone and oxides of nitrogen interfere with all three methods.

Zurlo and Grinnini (217) have studied the effect of oxides of nitrogen and heavy metals on the determination of sulfur dioxide by the absorption in tetrachloromercurate solution and then the reaction with fuchsinformaldehyde. It was found that o-toluidine eliminated the nitrite interference. Ethylenediaminetetracetate prevents the oxidation of sulfur dioxide by the iron present without interfering with the colorimetric method.

Goksoeyer and Ross (69) have developed a method for the determination of sulfur trioxide in flue gases by titration procedure. Steppuhn (186) has a patent on the continuous measurement of sulfur trioxide in gas mixtures. The apparatus uses thermal conductivity for the determination of the sulfur trioxide. The decolorization of thorium–eriochrome cyanine R lake is used by Zurlo (216) to determine sulfur trioxide content of the air.

Isopropyl alcohol is used by Stepanov and Puchkin (185) to absorb sulfur trioxide and sulfur dioxide. The sulfur dioxide is volatilized and titrated. The sulfur trioxide remains in the isopropyl alcohol and is titrated with standard caustic.

Hissink (90) traps out the sulfur trioxide by condensation and the remaining gas containing sulfur dioxide is scrubbed through hydrogen peroxide to oxidize the dioxide to trioxide. Chory (35) has combined the two preceding methods into one.

Carbonyl sulfide can be determined by absorbing in ethyl monothicarbonate and by microtechniques. Gamsjager (64) reports that in the absence of hydrogen sulfide and carbon disulfide, inorganic sulfides, thiosulfates, and thiocyanates act as a catalyst in the titration of the carbonyl sulfide with iodine. Golyand and Lazarev (71) determine both carbonyl sulfide and carbon disulfide spectrophotometrically. The gases are absorbed in alcoholic diethylamine and the diethylthiocarbamate and diethyldithiocarbamate formed are determined by ultraviolet spectrophotometry. Ciborowski, Przybylowicz, and Maciejewska (36) determine carbon disulfide spectrophotometrically by determining the absorbance of the carbon disulfide dissolved in benzene and hexene. Dutkiewicz and Jaszke (50) absorb carbon disulfide in alcoholic potassium hydroxide forming ethyl xanthate which is hydrolyzed to hydrogen sulfide and determined colorimetrically in the presence of ferric chloride and methylene blue.

Continuous determination of hydrogen sulfide in air is done by Chetkowska, Gallus-Olender, and Strzeszewska (34) by bubbling the air through a colorimetric reagent that can be regenerated by bubbling clean air through it. Delwiche (43) determines the optical density of a collodial lead sulfide formed by precipitating the lead sulfide from a solution by the sample containing hydrogen sulfide. A portable apparatus for measuring hydrogen sulfide is described by Smith, Jenkins, and Cunningworth (175), and a critical appraisal of five alternative methods for hydrogen sulfide is given.

Potentiometric determination of mercaptan sulfur in liquid hydrocarbons is described by Brejcha and Sima (25).

This method is devised based on the insolubility of silver mercaptide and silver sulfide in an ethanol solution. After comparing three methods of determining mercaptan in hydrocarbons. Romovacek and Bednar (157) state that the amperometric titration is the fastest, most precise, and most sensitive. The other two methods were potentiometric and colorimetry using p-aminodimethylaniline in the presence of an oxidizing agent. Sadijkhov and Korobtsova (161) also recommend the amperometric method for determining ethyl mercaptan.

CARBON DIOXIDE

The Orsat apparatus has been modified by Wronkowski (214) to determine carbon dioxide in air. The carbon dioxide is determined by measuring, with a 1-ml. micropipet, the difference in volume of air passed through potassium hydroxide.

A dry reagent made of activated alumina has been patented by Stanford (144, 184). Thymol blue is used in the tubes with the alumina to determine the concentration of carbon dioxide in air. The color change is blue-purple to pink. If diethanolamine is added in the preparation, the color change is blue to yellow. The reagent is insensitive to humidity and temperature.

Scholl (167) describes a simple device for the continuous determination of carbon dioxide in flue gas. The apparatus operates by comparing flow rates of the gas before and after the absorption of carbon dioxide in a suitable liquid. Comparison is accomplished by two manometers in series, with an absorption chamber in between. The flow rate decrease is proportional to the carbon dioxide content.

Tamont'ev (196) has studied the use of the TG-5 Titrimeter for the determination of carbon dioxide and gives the conditions best suited for its use under field conditions.

Lodge, Frank, and Ferguson (130) have determined the concentration of carbon dioxide in air by the variation in pH of a mixture of fine marble chips in distilled water through which air is drawn. Comparison with a calibrated nondispersive infrared analyzer showed excellent agreement.

A self-sampling indicator tube for carbon dioxide is developed by Kiff and Partridge (107). The tube contains rosaniline-HCl, sand, hydrazine hydrate, and magnesium carbonate. The tubes are stable for at least 1 year.

Lyutsarev (134) has designed a device for determining carbon dioxide for use at sea. Otsuka, Takahashi, and Yoshimura (151) have improved the conventional gas evolution method for carbon dioxide. Leithe (128) has worked with carbon dioxide in car-

bonates. Laux (125) has determined the carbon dioxide in samples from ethanolamine gas-treatment plants. Taranenko (198) has developed an apparatus for determination of carbon dioxide and ammonia in air. Stallechner (182, 183) holds patents on two apparatus for the measurement and determination of carbon dioxide in smoke gases and flue gases.

The construction and operation of a novel apparatus for the conductimetric determination of carbon dioxide after absorption in barium hydroxide are described by Milan (143). The carbon dioxide can be determined continuously without interferences from atmospheric carbon dioxide. The apparatus is suitable for soil, the respiration of seeds and bulbs, and determination of carbon dioxide in stored fruit.

CARBON MONOXIDE

Iodine pentoxide has long been used for determination of carbon monoxide. Klauer (112) suggests using radioactive iodine pentoxide and measuring the radioactive iodine produced by use of the Geiger-counter or ionization cham-Heidrich (79) in his patent describes a tube filled with a mixture of two silica gels. These both contain iodine pentoxide and oleum but one gel is shaken with dry iodine pentoxide and the other with an aqueous solution and dried and both are mixed with oleum containing iodine pentoxide. A well defined dark green zone appears when earbon monoxide is present. Filyanskaya (59) has determined the optimum conditions for obtaining indicating powder possessing a definite chemosorption capacity under the conditions of the analysis. Interference of hydrocarbons in the estimation of carbon monoxide by iodine pentoxide indicating is prevented by a protective layer of vanadium pentoxide, ceric oxide, or chromium oxide in the silica gel. Heinrich and Draeger (81) state that the protective layer indicates the presence of iodine by changing from vellow to grav. In their patent (84) they put a layer of activated charcoal either preceded or followed by a layer of molecular sieve before the iodine pentoxide oleum silica gel layer.

A cardboard that turns black in the presence of carbon monoxide and can be regenerated by exposing the card to atmospheric oxygen has been patented by Bangsgaard (8). Silica gel of 0.5 to 1-mm. particle size is treated with palladium chloride and capric chloride or ammonium nitrate solution. The yellow product is pasted on a yellow cardboard. Undesirable side reactions affecting the results of conventional carbon monoxide indicators can be minimized by covering such a reagent with a material which acts as a molecular sieve for carbon

monoxide. A film of polystyrene is given by Heinrich and Draeger (87) in their patent for this.

The determination of a trace of carbon monoxide in air in the presence of hydrogen by the intense color reaction with silver *p*-sulfamoylbenzoate is investigated by Ciuhandu and Krall (37).

Several methods of detection and determination of carbon monoxide are discussed by Darphin (42). He suggests for atmospheric control, apparatus employing iodine pentoxide or a complex silica-molybdate. For continuous atmospheric monitoring with alarm protection, it appears that infrared analyzers are the best.

Ovenden (153) describes a method for the continuous determination of carbon monoxide in air involving a vibrating palladium microelectrode intermittently polarized anodically while the air sample is passing through the cell. A limiting diffusion current is observed. This current seems to have a linear relation to the partial pressure of carbon monoxide in mixtures of carbon monoxide and oxygen.

An apparatus is described in a patent by Snelling (177) in which a catalytic carbon monoxide detector and its input gas are maintained at a constant temperature by steam from boiling water. The temperatures of the input gas and of the gas leaving the catalyst are measured by resistance thermometers; the temperature difference is calibrated in terms of carbon monoxide content of the input gas.

A method for the determination of carbon monoxide in the presence of hydrogen and methane is based on the combustion of the carbon monoxide to carbon dioxide in a stream of oxygen over copper oxide as a catalyst. Sverak (192) states that the oxygen serves both as a reactant and as a carrier gas. The catalyst is continuously regenerated. The end of combustion is determined by a potentiometric titration with barium hydroxide.

Dzedzichek and Demidov (51) also oxidize the carbon monoxide to carbon dioxide but this is done by passing the air through an incandescent platinum spiral. The carbon dioxide is absorbed in standard barium hydroxide. Korsh (118) burns the carbon monoxide with activated alumina as catalyst.

HALOGENS

Kindyakov, Shipirt, and Katlinskii (108) give a method for determination of chlorine, Cl⁻, HOCl, and H⁺ in the presence of each other. The method was deduced from equations for the calculation of the concentrations of the components involving the Lunge reaction and the constitution of chloride hydrolysis. Determination of chlorine

in mixtures with sulfur dioxide is described by Soloniewicz (178).

Vtorov and Kalmanovskii (210, 211) describe an automatic photocolorimetric gas analyzer for determination of chlorine in acetylene.

The sensitivity of a gaseous interferometer has been used by Strepikheev, Karetnikov, and Baranov (190) for determining hydrogen chloride in phosgene.

For determining hydrogen chloride in liquid chlorine, DeVries and Savariar (44) recommend absorbing the hydrogen chloride in a hydrochloric acid solution by passing the evaporated chlorine through 0.5M solutions of hydrogen chloride. The chlorine and HOCl are removed by refluxing.

The reaction of phosgene with hexamethylenimine is used by Terent'ev, Obtemperanskaya, and Buzlanova (200) to determine phosgene in the presence of chlorine and hydrogen chloride. Meisel and Mazor (141) pass the phosgene-carbon dioxide mixture through an 800° C. tube oven over silver to decompose the phosgene. The carbon monoxide formed is measured in an ozotometer.

Takai (195), to improve the conventional gas leak detector that uses a hot electrode to produce positive ions and therefore may not be used in an explosive atmosphere, uses a proportional counter as the detector by using air as the carrier gas for halide vapor, readily charged negative.

To develop a stable device that would serve both to detect and determine a gaseous tracer used for studies of atmospheric diffusion, Schultz (170) has undertaken an experimental investigation of positive ion production at heated surfaces. Freon-12 was used as the tracer. A G.E.-type H leak detector was modified to improve reproducibility. Halogen sensitivity is due to multiple-step process. Steps studied include thermal decomposition of the Freon, release of alkali from a heated source and transfer through the carrier gas to a surface at high temperature, ionization, and ion collection by an electrical field. Sensitivity may be lost in a somewhat irreversible manner by raising the halogen concentration.

Stack, Forrest, and Wahl (181) have refined the Funiwara pyridine-alkali reaction for the determination of trichloroethylene in air.

Vorob'ev and Chumicheva (209) describe the determination of hydrogen fluoride in the atmosphere in the presence of hydrogen chloride. The hydrogen fluoride is collected in water by aspiration; thorium nitrate, thoron, and hydrogen chloride are added, and the concentration of the fluoride ion is determined colorimetrically using a green filter.

A method is developed by Peregud

and Boikina (154) for determination of very small amounts of hydrogen fluoride in gases based on the formation of silicon tetrafluoride followed by the determination of silicon as a heteropoly acid.

AIR

Rykhter, Shlygina, and Kobyakina (160) have a universal absorber for determination of small amounts of harmful substances in the air. They use the absorber for sulfur dioxide, chlorine, hydrogen chloride, sulfuric acid, dust content, hydrogen sulfide, hydrogen fluoride, phenol, and phosphorus pentoxide.

Kitagawa (111) has made detector tubes for the measurement of toxic gases and vapors. The tubes are filled with the detecting reagent made of silica gel, alumina, or glass and impregnated with a detecting chemical specific for the gas to be determined. Heinrich and Draeger (85) have also been active in the making of detector tubes for indication of war gases. They also have a patent (82) for a gas-mask attachment for identifying toxic gases. A transparent attachment to the mask filter places an indicator paper in the air passage. Nonstable indicators are used in solution and are contained in a fragile vial which can be broken by finger pressure thus spreading the indicator on paper or other material.

Strange (188) describes automatic analysis of atmospheres. Instruments are based on measuring variations in thermal conductivity, density, heat of combustion, absorption of infrared or ultraviolet energy, and ionization properties. Specificity for selected stream constituents is sometimes achieved by special pretreatment or simultaneous measurements of more than one property of the sampled atmosphere.

An apparatus which operates on the basis of combustion of combustible gases or vapors in the atmosphere followed by measurement of the increase in temperature has a deficiency. Variation in the temperature of the incoming air and change in temperature due to variations in the voltage in the circuit feeding the platinum spiral are not taken into account; this causes inaccuracies in the readings for the apparatus proposed by Giber, Tamas, and Devay (66). These sources of error are eliminated since the apparatus operates on a differential principle measuring the difference between the temperature of two chambers connected in series and heated uniformly by the platinum spiral. In the first chamber the combustible gases or vapors contained in the air are burned. The combustion products are then fed to the second chamber after cooling to the temperature of the incoming air in a

special heat exchanger. This apparatus is intended for determination of the content of, for example, methane in the air of mines, and the concentration of gasoline, ether, acetone, and other vapors.

Jones et al. (100) state that no single instrument can measure all of the hydrocarbon components in automobile exhausts. The flame ionization hydrocarbon detector, the infrared spectrophotometer, and the gas chromatograph case measure most of them. The flame ionization hydrocarbon detector can measure total hydrocarbons while the nondispersive infrared instrument will measure saturated hydrocarbons. The difference between the two is a measure of the unsaturated hydrocarbons.

Lugg (133) gives a colorimetric method for the determination of phosphine in air based on its simple and sensitive reaction with silver nitrate impregnated paper. Printed stains have been prepared and calibrated for field estimation as standards for dry papers, since these give an ever-reproducible stain and are easier to handle than wet papers. The calibrated stains were made from concentrations of phosphine determined by using the silver diethyl-dithiocarbamate reaction.

WATER

Friedman and Talbot (62) have patented a dew-point indicator which is a modification of a dew-point apparatus of a combination of an optical-electrical servosystem and thermistor for measuring the temperature on a mirror surface. To this have been added an ultraviolet source with strong emission at 1216A., a magnesium fluoride—coated aluminum reflective surface, and an ionization chamber sensitive to such reflected light and adapted to produce an output signal relative to light reflected.

A study of synthetic zeolites as molecular sieve absorbents by Hybl (94) and Jantula shows that zeolite with univalent cation silver and bivalent nickel or cobalt cations belong to a class of compounds that change color in the presence of water. Silver zeolite contains no sodium because sodium ion readily exchanges quantitatively for silver. Nickel and cobalt zeolites contain traces of sodium. Their ability to indicate moisture appears when the ratio of nickel and cobalt to sodium is 1 to 2. The colors of the dry zeolite and the zeolite exposed to various moisture concentrations are tabulated.

When determining water by the Karl Fischer reagent, Otterson and Fryburg (152) recommend the coating of the rubber s'eeve enclosing the collector with Dow Corning silicon stopcock grease and coating all joints with red Glyptal instead of paraffin. They claim

this will decrease the blanks by one third.

Muroi (145) has improved the Karl Fischer apparatus for microdetermination of water in gaseous sample. Good precision and speed are claimed.

The determination of traces of water in liquid ammonia has given trouble for many years. Klingelhoefer (113) has developed a coulometric method using the electrogeneration of potassium in liquid ammonia to determine water. The sample of liquid ammonia is passed through a potassium chloride tube into the cathode chamber. The end point is determined by an increase in the electrical conductance of the solution, and this automatically terminates the generating current. Good results also are obtained by using the blue color of the excess potassium ions as the end point. A platinum cathode and an isolated carbon anode are used.

Water in hydrogen fluoride is usually determined by Karl Fischer reagent. Wejnar (212) has developed a conductometric method for measuring water in the absence of sulfur dioxide concentration. Ukaji and Kageyama (207) have determined the relation between the water content of anhydrous hydrogen fluoride and its specific resistance measured by the Kohlrausch bridge.

The electrolytic cell using a film of phosphorus pentoxide for the absorption of moisture present in gas is used in several instruments. Rath (156), Karpov et al. (104) and Halter and Johnson (74) have studied this procedure; they have made application of the principle in a particular stream. Modifications have been made for their individual problems.

Water can be determined in gas by reacting the water with calcium hydride and measuring the hydrogen produced. Gol'dinov, Lukhovitskii, and Srubinskaya (70) have improved the conditions and apparatus for water determination. Forbes (60) and Abrams and Smith (1) have used the same procedure but have converted the water to acetylene and then used an infrared analyzer for determination of the acetylene.

Measurement of water content of gases by hygrometers and modifications for more accurate determinations are described by Barendrecht (10), Baumann (12), and Brasseur, Gargasson, and Perilhou (24).

HYDROCARBON

For determining small amounts of acetylene and methyl acetylene in gases, Pribyl and Soucek (155) make use of the ultraviolet absorbance of soluble silver complexes of acetylene and methyl acetylene. To determine acetylene in air, a measured volume of gas is passed through silver perchlorate. The absorbance of the acetylene complex is

measured immediately. For methyl acetylene in propylene, a measured amount of propylene is passed through the silver perchlorate, and the methyl acetylene complex is measured after removing the propylene by heating.

Acetylene did not show its own reduction wave in the ordinary region under -3.0 volts. Therefore, Usami (208) has caused acetylene and mercuric acetate to react to form a mercury addition compound. Its polarographic determination was investigated, and a rapid and simple method was established.

Korsh (117), for the determination of trace concentrations of acetylene in gaseous mixtures, passes the air over pieces of glass or porcelain in a container kept in a Dewar flask to adsorb the acetylene. This is then desorbed by raising the temperature and sweeping with a hot stream of nitrogen into absorbers. The amount of acetylene is determined colorin etrically.

Turbidimetry, infrared absorption spectrometry, and ultraviolet absorption spectrometry are compared by Hata (76) for the determination of divinyl acetylene in acrylonitrile. From his findings he states that ultraviolet spectrometry was the best method of analysis of the three.

Klylova (114) has collected ethylene in sulfuric acid by aspiration, added metaperiodate, and determined the formaldehyde formed colorimetrically using chromotropic acid.

Bellen and Kochel (14) used 2,4-dinitrophenylhydrazine for determination of acetaldehyde. They (15) also suggest potentiometric titration with glass or antimony and calomel electrodes. For potentiometric determination, they suggest using potassium iodide with silver or mercurous sulfate electrodes.

A colorimetric method with fuchsin reagent was proposed by Hata and Okada (77) to determine acetaldehyde and methyl vinyl ketone in acrylonitrile.

Altshuller (5, 6) describes the coulometric method for determination of olefins using the Model 811-1 from Mast Development Co. The instrument was used to measure pure olefins in artificial mixtures and in automobile exhaust. He also describes the determination of olefins by reaction with p-dimethylaminobenzaldehyde in sulfuric acid. Nicksic (147) also uses the coulometric titration for olefins.

The mercurimetric method for the determination of isobutylene is described by Markevich (137).

Photometric determination of small amounts of butadiene is described by Tsekhanakaya (206).

The separate determination of benzene and toluene in air in the presence of xylene is given by Kachmar (101). This is achieved by separate determination of benzene and toluene and com-

parison of the results with a series of similar tests on mixtures of benzene and toluene of various composition. The method is based on obtaining nitro compounds of benzene and toluene and their reduction to amino compounds which are then diazotized and combined with selected substances to form azo dyes.

A complex ionization apparatus is described by Krivitskii and Krigman (120) for separate determination of carbon dioxide and methane in mine atmosphere. Two ionization chambers, one for comparison, are located in the measuring unit. The volume of the chamber is determined by a collecting and a high-voltage electrode. Each ionizing radiation source is a stainless steel dish coated with an inorganic enamel containing plutonium-239.

MISCELLANEOUS AND APPARATUS

A sensitive stable vapor detector based on response to changes in dielectric constant is described by Winefordner, Steinbrecher, and Lear (213). The detector consists of a variable capacitor mounted in a special cell which allows gas to flow between its plates. If the difference frequency between oscillators is adjusted to zero with a pure carrier gas flowing through the cell, the presence of an impurity vapor produces a difference frequency which is a linear function of the concentration of the original liquid introduced into the cell via the carrier gas. The detector response is extremely rapid and nearly insensitive to high carrier gas flow rates and variations in flow rate.

A new mass-spectrometer leak detector is investigated by Cossutta and Steckelmacher (39) based on the use of an axially iron-shrouded system with magnetic lens for focusing ions in the low mass range. By taking precautions to keep the H background at a low and stable level, it was possible to use hydrogen as a search gas.

Lange and Lippold (124) give a simple and sensitive adsorption device for detecting leaks of gases with very low condensation temperature using an adsorbent such as silica gel cooled to the temperature of liquid nitrogen. A Pirani gauge, simpler in construction than the Penning vacuum meter, is used.

Use of a charcoal trap by Ishiĭ (98) removes the need for use of liquid nitrogen or air. Sensitivity is improved by use of an a.c. amplifier in the system.

Any apparatus for the detection of the gases escaping from drilling muds is essentially a modified Wheatstone bridge. The design and theory of operation of the apparatus are discussed by Csokas (41). The apparatus is used primarily to show, in drilling for oil, when a gas- or oil-containing

stratum is reached and the thickness and depth of the stratum, the depth and thickness of a coal deposit, and the methane content of mine gases; it is also used for the control of the atmosphere in industries that treat or produce hydrocarbons.

Botden (23) describes the silica gel leak detector consisting of a sensitive Penning gauge connected to a tube filled with silica gel grains cooled to liquid-air temperature.

A leak detector, sensitive to sulfur hexafluoride, can detect 1 part in 107 by volume of sulfur hexafluoride in air. The apparatus is applicable to the detection of leaks of electronegative gases used as gaseous dielectrics in high-voltage devices and as arc-quenching media in circuit interrupters. For such applications, the gas is usually sealed in the devices at pressures exceeding atmospheric. Operation of the apparatus is based on the difference among gases in the rates of electron attachment at low electron energies to form negative ions. The apparatus is described by Fox, Malmberg, and Gosser (61).

A description is given by Doctoroff, Grossel, and Oblas (47) of an experimental helium mass spectrometer capable of detecting leaks.

A simple, inexpensive, highly sensitive gas detector is patented by McAfee (139). The detector is based on the diffusion principles and consists of a gastight mantle which is closed at one end with a gastight cap and surrounded by a heated wire. Many glass tubings closed at one end are placed into the mantle which has a gas inlet and outlet. The other end leads into a gastight chamber which is limited by a portion of the gastight mantle. The chamber is connected with a detector element which reports the gas diffusing through the glass tubing. The detection of gases is based on the selective sensitivity of thin-walled glass.

Nonlinearity of the flame ionization detector at high concentrations caused by inefficient ion collection, owing to ion recombination and space charge effects, can be overcome by using a flat probe electrode which subtends a large angle at the jet, or a hat-shaped collector in conjunction with an adequate probejet voltage. A nonlinear response system to avoid sensitivity changes with wide range samples is described by McWilliam (140).

A new type of laboratory gas viscometer, formed by two flowmeters arranged in series, is given by Caffo (32). The upstream and downstream flowmeters contain a capillary tube and a central porous plate. When the pressure drop through both flowmeters and the density of the gas are known, the viscosity of the gas relative to air can be calculated.

A colorimetric instrument for the determinations of traces of components in gases is described in detail by Lada and Wassak (123). The main advantages of these devices are simplicity of construction and materials, easy adaptability to various components and to different concentration ranges, operation in closed circuit, thus reducing the sample size, and the determination of the components as pure gases, thus permitting easy and rapid calibration and verification of accuracy.

The gas density balance of Martin and James is discussed by Johnson, Childs, and Beaven (99).

A simple and accurate method of pressure control is described by Edge-combe and Jardine (54) for studying gas reactions under conditions of constant pressure. It is capable of automatically maintaining the pressure to within 0.01 cm. of mercury and of providing a continuous record of the volume change with time. A glass spiral manometer is used to measure the pressure change.

A novel bubbler is described by Kamphausen (102) for the microdetermination of gases. The design is based on the well known rod and disk principle. The distance between the outer edges of the disks and the walls of the bubbler is critical. A float valve disperses the gas and allows continuous cycling of the absorbing liquid.

A syringe adapter is designed by Giroux, Hahto, and Pollak (68) to permit minimum dead volume and assure reproducible volumes for gas injection.

A device containing a bladder and four syringes in combination is described by Lacy and Woolmington (122) for use in the preparation of accurate standard gas mixtures.

Alikin (4) has developed a microburet with continuous recording of the change in the gas volume operating on the principle of a potentiometer. A mercury globule slides in a capillary between two parallel Nichrome or platinum filaments to one of which is applied a constant voltage. The position of the drop depends on the gas volume.

A patent by Leisey (126) is for a titration cell equipped with a magnetic stirrer and drain valve with one set of electrodes for coulometrically generating a titrant at a constant rate and a second set for amperometrically detecting the preselected reference titrant concentration.

Barendrecht and Martens (11) describe a completely automatic coulometric titration apparatus for process use.

An ionization-type indicator for methane with a tritium radiation source is given by Gorlovci (72). Tritium absorbed on zirconium or titanium presents the following advantages: long half

life, low cost, stability of the compound with the metal, high specific activity, and a short free path in air. The device can be safely used under industrial conditions

An omegatron is constructed according to the design of Alpert and Buritz. The theory of the omegatron is outlined by Masica (138) and schematic diagrams of the apparatus and the electrical wiring are given.

Meyers and Martin (142) describe a low temperature infrared gas cell of simple construction.

An apparatus is described by Oster (150) for use in estimating the proportion of gases or vapors with electrical dipole structure in mixtures with other gases not having this structure.

The analyzer for inert gases described by Nashempa and Lakomskii (146) operates by absorption by calcium vapors of active gases present in an inert gas used in electric welding. The calcium vapors and calcium sublimates deposited on the walls of the reaction flask react with argon impurities forming calcium nitride, oxide, hydride, and hydroxide. The amount of impurities in argon is calculated from the pressure established in the flask after cooling to the initial temperature.

Sunberg's (191) patent describes an apparatus comprising a transparent measuring tube with a calibrated seal which has upper and lower flared sections, the upper section with a cover functioning as a gas chamber and the lower a reservoir containing an absorbent liquid. The cover of the upper section is fitted with a valve to control the admission of the gas to be analyzed. The lower section is closed by a flexible diaphragm, fitted with an annular apparatus with a threaded opening containing a threaded perforated plug engaging the diaphragm to control the liquid level in the measuring tube.

The patent of Skarstrom (171) gives an apparatus especially useful for determination of key components in refinery gas streams. Noebels (149) has a design for automatic trace analysis. Hummel's (92) patent is based on the measurement of dielectric constant (the analyzer consists of a measuring condenser on a cavity resonator containing the material to be analyzed), changes in which produce an alternating flux which is amplified and fed to an indicating or recording instrument. A periodic change of conditions could be produced by a piston or a change in controlled gas flow.

Heinrich and Draeger (83) have patented a recording apparatus for determining gas constituents. Successive analyses for a given constituent in gases are made by use of a magazine with a series of tubes open at both ends and containing a suitable reagent. These tubes are normally closed by

spring pressure on both ends, but are brought successively to a location where the gas passes through the tube for a definite time period.

Drawin's (48) patent is an apparatus for continuous analysis of gas mixtures. By successive absorption of gas components in a gas mixture, the differential back-pressure method can be adapted to rapid continuous analysis by converting the deflections of diaphragm gauges into electric currents. These currents are monitored by recorders.

The apparatus of Block and Schlenz (18) avoids the error, common to gas analysis methods, of limited measurements of pressure fluctuation. The device contains an auxiliary circuit from a potentiometer resistor fed by a converter yielding an electric output as a function of the pressure. By rating the tapping resistance, an automatic compensation of measuring errors due to pressure fluctuations is achieved at any point of the total measuring range. For all pressure fluctuations and concentrations of the component to be measured in the test gas, a correct value is obtained for all scale points on the indi-

Spracklen, Campbell, and Fellows (179) have patented an apparatus consisting of a rotating electrode, partially immersed in a solution. The electrode is made of a material inert to the electrolyte and the gas sample. The apparatus acts as a concentration cell to effect a change in the ionic content of the solution and to pick up one gaseous element in parts per million.

An electrolytic device for the determination of reducible gas in solution has been patented by Carritt and Kanwisher (33). The portable device is provided with an electrolytic probe which contains at least two metallic electrodes adjacent to an electrolyte-absorbing carrier enclosed in a plastic envelope. Further, the electrodes and the carrier are enclosed in a plastic membrane permeable to the reducible gas but impermeable to dissolved salts. One of the electrodes is used as an anodic reference electrode.

Gas analyzers are described by Ebbinghaus (52) for measuring the constituents with paramagnetic susceptibility, especially of oxygen, in the gas under test. The analysis cell consists of a small tube surrounded by a heating winding, the ends of the tube being connected to a divided lead carrying the gas under test and the tube with the heating winding being arranged in an inhomogeneous magnetic field. A means of adjustment is provided for suppressing the zero point in such a way that the deviation of the oxygen content in the gas under test from an adjusted value can be measured.

A method of increasing the sensitivity of an optical-acoustical gas analyzer is described by Gerlovin and Slobodskaya (65). The method is based on the use of cuvettes designed for multiple passage of radiation within the cuvettes by means of mirrors. A double beam instrument is used. The dependence of signal strength on the effective thickness of the layer of absorbing gas in the cuvettes is studied.

Procedures used for the determination of trace impurities in chemical products are described by Hanes, Sandulescu, and Lupu (75). Methods described are coulometry, potentiometry, conductimetry, polarography, absorption spectrophotometry, x-rays, emission spectroscopy, activation analysis, and chromatography.

A modification of the McLeod gauge that was the variable compression method of analysis is described by Hayward (78). By heating the capillary and gauge above the condensation temperature of all components, fairly accurate results can be obtained.

Colombo (38) gives an apparatus for degassing water and for collecting and measuring extracted gases. which must be degassed drops in a flask and is distilled in vacuo by the use of a mercury diffusion pump. Water is frozen by two liquid air traps while the permanent gases are extracted by the diffusion pump. A Toepler pump collects the permanent gases and measures them at room temperature.

After a discussion by Bergshoeff (17) of the requirements for an absorber and of the factors determining the efficiency, a new absorbing device is developed. The construction of the apparatus and its performance are described.

Bunich, Voinov, and Tomasheva (31) discuss sampling of gases for analysis. The apparatus for sampling gases at high velocity avoids a direct connection with a vacuum pump. Four aspirator vessels are connected by valves to the gas-sampling tube. The outflow of the liquid from the vessels is regulated by cocks, leading through a tube to the opening near the bottom of a large flask; at its mouth, this flask is connected with an ejector pump. Operation of the ejector accelerates the outflow of the liquid from the aspirator vessels to the flask and the sampling; the samples can be taken in quick succession.

The application of the Orsat apparatus to the analysis of flue gases is described by Ebersbach and Ruch (53). The relative merits of various absorbents are discussed. Frequently encountered sources of error and the manipulation of the apparatu are described in detail.

Fluctuations of the indicated output of gas analyz rs of the thermal-gradient flow type that are caused by atmospheric variations are compensated by means of a liquid-filled metal bellows. This compensator makes use of the fact that an increase in pressure will increase the indicated output of the analyzer, and an increase in temperature will decrease the indicated output. The compensator controls a heater that varies the ambient temperature of the gas analyzer cell and thereby offsets errors caused by pressure variations (203).

Smith and Merritt (176) discuss a negative ion gas analysis technique. A three-electrode gas ionization chamber was used to detect gases. Auxiliary equipment included an electrometer and a strontium-90 source within the chamber to ionize the gas. An a.c. potential applied to the grid modified the cell characteristics or canceled background current. Trace amounts of electrophores in gas streams whose primary constituents do not ionize may be measured quantitatively.

A method for volumetric gas analysis is described by Schulek and Pungor (169), in which a specially designed apparatus is used to transfer aliquots of a gas mixture at known temperature and pressure to a reaction flask. A suitable reagent is added for the component sought. After the reaction is complete, the weight of the gas component which reacted is determined titrimetrically or microanalytically. The method can be used with good accuracy for determining trace components in gas mixtures.

Kusler (121) has developed an improved gravimetric method for analyzing blast furnace top gas and is applicable to other gaseous mixtures. The mixture is passed at a controlled rate through a low cost analytical system, and all of the components except nitrogen are determined gravimetrically as carbon dioxide or water or both. The residual volume of gas finally exits through a wet test meter and is determined by direct measurement.

By using an apparatus in which liquid flows slowly as a continuous thin film over a metal electrode, classical electrochemical methods such as amperometry, differential titration, and polarography, can be applied to the continuous analysis of gases containing volatile acids, bases, carbonyl compounds, and alcohols. Lestienne (129) reports that the response is instantaneous and the method highly sensitive.

A new method of gas analysis based on the postluminescence of air is reported by Krapivin and Andreeva (119). The method is based on the decrease in postluminescence of air when the concentration of impurities increases. The apparatus consists of a discharge tube with three zones: a discharge zone into which gas flows through a capillary tube during evacuation, the tube being fitted with external electrodes; a cooling zone; and a luminescence zone, in which the light intensity decreases along its length.

Instead of collecting a combustible

gas in vacuo, the evolved gas is carried away by a stream of inert gas and is led through a combustion chamber where it reacts with oxygen (88). The residual oxygen leaving the combustion chamber with the carrier gas enters an oxygen measuring device that continuously indicates the concentration. The time integral of the difference of two oxygen concentrations can be used to calculate both the rate of evolution and the total quantity of combustible gas evolved.

The analysis of residual gas in electron tubes is described by Frost (63). The method is devised for small tetrodes or pentodes. In contrast to other methods, the composition of the gas is not changed markedly by the analysis. The analyzer is made of Corning 0120 glass with a conductive lining.

The physical principles of the operation of thermomagnetic gas analyzers involves the following (56): The magnetic susceptibility of oxygen is two orders higher than that of other gases; it decreases with increasing temperature. If a heated body, a sensitive element, is placed in a certain space within a nonuniform magnetic field, and an oxygen containing gas is let into this space, then the gas will be attracted to the magnetic field with a force proportional to the magnetic susceptibility. A cold gas is attracted to the magnetic field with greater force than a heated gas near the sensitive element. This produces a gas current in which the heated gas is continuously replaced by the cold gas. The gas current cools the sensitive element, which is metal, and has a high temperature coefficient of resistance. Since the rate of the gas current is determined by the oxygen content of the gas, a change in the electrical resistance of the sensitive element is a simple function of the oxygen content.

A new method and apparatus for the determination of the particle size of aerosols are described by Strauble (189). The droplets are suspended in an electrical field for a prolonged period. The particles are surrounded only by gases, and their behavior, with regard to speed of evaporation, can be observed accurately. Observations on the condensation or crystallization of droplets can be made. The size of the droplets can be observed continuously by means of the light which they disperse.

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