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[End of Review Section]

Automatic Operations in Analytical Chemistry

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THE automatization of analytical chemistry described a year ago (*359*) appears still to be accelerating with the climax not yet in sight. The volume of literature describing new laboratory and industrial developments and applications is so voluminous as to challenge seriously the ability of any one person to keep abreast of this rapidly moving phase of quantitative analysis.

The period covered in this review is essentially confined to the past two years, inasmuch as the literature search for the previous review was terminated late in 1948. Again emphasis is laid on the fact that the very desirable end of completely eliminating the human factor in the gathering of quantitative measurements is rarely attained. The analogy between the breakdown of chemical engineering processes into unit operations and a similar classification of analytical methods is continued.

The desirability of measuring physical properties automatically has been evident to man ever since the science of measurement first began. This is partly a result of man's innate interest in the novel and unique. This was the case, no doubt, with Pharaoh Ptolemy's fascination in Hero's Automaton dating from 200 B.C., which was one of the mechanical marvels of ancient times (*62*). Far from a simple whim, however, is the chemist's present interest. The necessity of obtaining extensive amounts of data accurately and economically has forced the adoption of instruments which will perform the required operations with a minimum of human effort.

The role of physical properties becomes even more obvious in a study of automatic operations in quantitative analysis. Numerous authors have emphasized the increasingly close interdependence of physical properties and modern analytical chemistry (*22, 146, 335, 403*). A number of books have been published recently on physical methods and instrumentation (*28, 34, 140, 464, 472*). In fact, a scientific instrument has been defined as any system which gives numerical approximations of the true magnitude of some physical property. The commercial literature available from American instrument manufacturers is frequently a good source of fundamental information (*329*). A number of firms regularly publish news-style periodicals which are available free.

Not all comments on this trend toward automatization are favorable, however. A number of authors, particularly Hammond (*203*) and Yardley (*478*), "deplore indiscriminate instrumentation" and warn "how fatally easy it is to become a slave to one's instruments." Their stand in regard to automatic control is that "it is tireless, but also brainless, and cannot anticipate or profit by experience." Others in this country, though less harsh, advise critical examination of the degree to which specialized instruments can meet certain problems (*204*) and discuss the factors determining the validity and integrity of the results obtained (*84*). Lack of specificity of physical properties and frequent insufficient sensitivity are other criticisms (*334*). On the other hand, the number of reviews on automatic analytical measurements and process control systems leaves little doubt of their importance (*59, 75, 157, 206, 320, 363, 373*). The review by Gildersleeve (*186*) is especially good for its schematic diagrams.

A recent lengthy review by Faĭnberg (*151*) on modern methods of automatic gas analysis describes a similar automatization trend in Russia. Faĭnberg makes frequent reference to the disadvantages imposed in this field in countries outside the iron curtain by "the capitalistic masters" and criticizes the patent system. He does, however, describe in some detail ten classes of automatic gas analysis with several German and Russian examples of each type. Most of these are used, at least in modified form, in this country. Although the reviewers have translated the paper in its entirety, space here does not permit its abstracting in detail.

One major trend in the past few years seems to have been that of perfecting existing fundamental methods with a view to increasing the reliability of the data obtained. As Churchill has pointed out (*84*), the standards on which calibrations are based depend on laborious and time-consuming traditional methods. Consequently, improving classical methods becomes more important, as their actual use in routine work diminishes. More attention is being given to simplified operation and maintenance. This desirable trend is exemplified in a recently marketed light-scattering microphotometer (*330*). The controls on this device have been so designed that no adjustment of them can result in damage to the various circuit components. It also has phone-jack connections for hooking up to any commercial direct current millivolt recorder.

Whenever possible, expedients in economizing the development and use of automatic analyzers have been used—for example, there is increasing use of a central measuring element to handle samples from various different locations. This involves sequential sampling programed automatically and gives periodic rather than continuous analysis. Although this complicates the sampling problem, substantial savings can result. Again, basic components which may be used for various purposes may be incorporated physically into one apparatus, as has been done in Lingane's multipurpose electroanalytical servo-instrument (*292*).

Cost factors involved in automatization were considered at a recent instrumentation symposium (*77*). Several instrument companies have cooperated in the development of expensive equipment with large industrial laboratories and then placed it on the market without restriction to all users at reduced cost. The problem of disseminating information and practical experience to students and potential users is being solved in some cases by special short courses offered by instrument manufacturers (*45, 322*) and a few educational institutions. Simple demonstrations in exhibits set up at conventions and meetings are desirable, but hardly adequate. Müller's suggestions (*329*) for more effective education in contemporary instrumentation demand consideration.

THE SAMPLE

Three types of operations on the sample still appear to be necessary, despite the very great desirability of avoiding these by making the measurement directly on the material in question. Automatic means for sample selection and preparation, sample measurement, and preliminary sample treatment continue to be developed and used as parts of the over-all process of analysis.

Improved methods for handling samples generally combine selection and sample measurement in one operation, or at least in one piece of apparatus. An interesting, although rather specific, sampling arrangement (*372*) for gases has been described in a patent for an "odormeter" which involves continuously diluting a stream of the gas with pure air and carrying the mixture to a "region confining the nose of the operator." The amount of dilution is increased until a threshold value is obtained. A commercially available "alcometer" (*2*) for testing the alcoholic content of a suspect's breath collects a 30-ml. sample requiring "a minimum of cooperation from the subject." Automatic timing circuits cause a blower to clean the system with air for the next test. Rahn *et al.* (*383*) have described an apparatus for automatic sampling (and continuous analysis) of alveolar air during normal respiration with an aviation mask. Four papers describing gas samplers include a continuous collector which draws a sample proportional to the main line flow (*386, 402*), a device for automatic delivery of gas samples to an Orsat gas analyzer (*177*), and a gasometer with automatic compensation for excess pressure (*82*). The gasometer operates by having the displaced water flow into an auxiliary reservoir connected temporarily to an evacuated chamber. This connection is made by a relay-actuated motor-driven stopcock which is turned on or off by a small mercury manometer. The height of an electrical contact in the manometer can be adjusted for different sensitivities. Settings can be fixed within 0.1 mm. of mercury for gas flows up to 300 ml. per minute. Various automatic smoke samplers use modern fluid or pneumatic differential pressure controls or small blowers, thus separating the solid particles on filter paper (*15, 124, 455*) or electrostatically (*316*). Another electrostatic sampler (*399*) continuously collects sulfuric acid aerosols and other air-borne particulate electrolytes followed by conductometric measurement.

Liquid samplers have been specially designed to prevent pump damage (*267, 315*) and to perform special jobs (*326*). An automatic apparatus for feeding liquids at rates from 0.1 to 3 ml. per hour has been described (*152*). Automatic collectors for samples from distillation or ion exchange columns (*312, 431*) and a liquid drop counter for sterile solutions (*298*) have also been developed. Another sampler for liquids described by Phillips (*366*) consists of a receiver which is depressed by the weight of the fraction coming off a chromatographic column. As the tube fills, it lowers until it is low enough to pass under the tip of an aluminum retaining strip. A tension spring then causes the circle of receiving tubes to rotate one position. The impact of the next tube against the retaining strip can be made to activate a recording pen.

Recent developments in collecting liquids simultaneously at different depths (*258, 416*) have been announced. One sea sampler (*416*) has 12 sample bottles attached to a bathygraph arranged to trip at prechosen pressures.

The sampling of solid materials such as fuels and grains traveling on conveyer belts can be handled by using a sample cutter moving at right angles to the line of flow (*208*) or by a pipe-type sampler which can take a series of very small increments from the material stream (*452*).

Treatment of the sample is avoided whenever possible, but certain operations are frequently necessary—for example, analysis of radioactive substances must sometimes be handled through automatic remote control devices (*438*). These have also been covered in a review by Curtis (*107*). Taxwood and Stock (*428*) have developed an apparatus for controlled uniform rise of temperature involving a variable transformer driven by a clock-type synchronous motor. Numerous devices for automatic combustion of organic samples (*156, 443, 444*) have appeared in the literature, some involving movement of the electric furnace

(*349*, *394*, *397*) or microburner (*449*) or the combustion boat itself (*125*). One such device (*87*) even has a timer to turn on the heater 1 hour before the operator arrives each morning. Induction heating has been used in a recently commercialized semiautomatic carbon in steel analyzer (*162*).

THE DESIRED CONSTITUENT

Once the sample is obtained, separation of either the desired constituent or interfering constituents may be necessary.

Automatic methods of separation include precipitation, filtration, sedimentation, volatilization, extraction, sorption, electroseparation, and magnetoseparation.

Filtration of analytical precipitates still is not done automatically, although one paper on the automatic washing of precipitates has appeared (*279*). Solid particles in air may be filtered automatically for smoke analysis through small disks of filter paper (*15*), continuously moving filter paper tape (*455*), or filter bags (*124*). Continuous dialyzers are described in Skeggs and Leonards' recent work on artificial kidneys (*409*, *410*) and in a Swiss patent by Signer (*408*). Gaseous filtration of everything but the desired constituent by permeation through a palladium sleeve is the basis of a hydrogen meter patented by Watson (*460*).

Sedimentation is used as the means of separation in an automatic machine described by Cullen and Marshall (*106*) for determining clay substance in molding sands, while a continuous centrifuge has been shown by Jasmund (*249*) to be useful for determining the distribution of suspended matter.

Separation by volatilization of substances with sufficiently different vapor pressures continues to be a useful method. An automatic still is described (*358*), as is a distillation apparatus for gasoline analysis with automatic control of reflux ratio and size of fraction (*420*). A gas thermometer with a mercury manometer contact arrangement has been applied to the separation of gases by isothermal distillation (*441*). The temperature control is within 0.3°. Continuous fractionation (*37*) and small scale superfractionation (*172*) columns are finding use for petroleum products. An automatic steam distillation apparatus (*389*) which is particularly applicable for Kjeldahl determinations has the receiver sitting on a pan supported by four springs. As the receiver fills up, the pan lowers under the increased weight until it activates a contact switch which turns off the electric heater and sounds a buzzer.

The removal of water from solids is the object of two laboratory devices, one (*424*) of which is a dryer for the continuous determination of moisture loss. Air is blown through a slide valve past an electrical resistance heater and then past the sample which is suspended from the arm of a balance. Freeze drying, or selective absorption heating, is convenient for heat-sensitive materials (*382*). The water sublimes off without going through the liquid state.

Liquid-liquid or liquid-solid extraction is such a common method of separation that considerable automatization has been accomplished. Schechter and Haller's percolator (*400*, *401*) for ether extractions of plants, Lowe's continuous extractor (*299*) for the determination of theobromine in cocoa, and Nolan's multiple extraction apparatus (*348*) are examples. The latter can handle up to 54 analytical extractions simultaneously. Chute and Wright (*85*) have designed a continuous extractor for high pressures. Improvements in countercurrent distribution apparatus have been developed by Craig and Post (*103*, *104*) and by others (*354*, *384*).

Sorption methods of separation include both adsorption and absorption of liquids or gases. The absorption of carbon dioxide by sodium hydroxide is the basis of a testing apparatus (*115*) for measuring the carbon dioxide produced by plant respiration. Others include an automatic absorption vessel for gas analysis (*198*), an adsorption balance for plotting rates of adsorption of a gas by a solid (*150*), and a carbon monoxide indicator (*457*) where an air sample is pumped through activated carbon to remove heavy hydrocarbons, then through silica gel or alumina gel to remove water, and into a cell containing a hopcalite–silica gel mixture where the carbon monoxide is oxidized and absorbed. Laboratory evaluation of oil deterioration can be handled by an 8-unit automatic oxygen absorption apparatus (*281*). Absorption of water by thin electrolytic films—e.g., phosphoric acid—followed by conductivity measurement, has been accomplished (*462*). Automatic paper chromatography can be accomplished with an automatic instrument developed by Müller and Clegg (*332*) to record continuously the process of separative diffusion of microgram quantities through special paper matrices.

Separations involving the flow of an electric current include mainly electrodeposition. A number of recent papers describe successful analytical applications of controlled potential electrolysis (*271–273*, *278*, *293*, *362*), especially with mercury cathodes. This technique is useful for separations of metals prior to coulometric or polarographic analysis. Lamphere and Rogers (*278*) made an instrument employing mechanical regulation of the potential, because it can extend to current ranges of 1 ampere or more, a situation which would require more cumbersome apparatus if handled electronically. On the other hand, a potentiostat recently announced by Lingane and Jones (*295*) operates from 110-volt alternating current to give an output up to 5 amperes at 6 volts. It features either cathodic or anodic potential control with a sensitivity of ±0.01 volt. The direct current voltage is set by means of a Variac transformer on the alternating current input side. Kovalenko's device (*271*) controls the minimum current by means of a photo-relay which is activated by a light beam reflected from an aluminum foil reflector on the needle of a milliammeter in the deposition circuit. Other electrical methods of separation include a commercial electrostatic smoke sampler (*316*), based on the Cottrell principle, which can collect up to 200 mg., and a continuous electrophoretic separator (*427*) for flowing liquids. A recently announced electrical method for separating charged particles (*25*, *79*, *331*) (designed for cations, but adaptable to anions also) is analogous to mass spectroscopy. Instead of bending the path by a magnetic field, a radiofrequency potential is used to accelerate the ions, different masses acquiring different speeds. It can sweep twice a second through the mass range of 10 to 50 and the data can be shown directly on a cathode ray oscilloscope or as galvanometer deflections. Its sacrifice in range and precision is balanced by its compactness, which permits its use in continuously analyzing the upper atmosphere from rockets. The Bureau of Mines is finding it useful for field determination of low percentages of hydrogen in helium, and states that it could be an extremely sensitive carbon monoxide detector.

Improvements continue in magnetic separations using the mass spectrometer (*42*, *97*, *180*, *240*, *476*). Modified designs are available for leak detection with helium as the tracer (*447*) and for detecting small amounts of impurities in metal (*159*, *466*). Particular applications of mass spectrometers for continuous analysis have been described, particularly a "drunkometer" for analyzing the alcoholic content of a person's breath (*63*), a combination method together with infrared techniques for light hydrocarbon analysis (*355*), and models for mixtures of carbon dioxide, oxygen, and nitrogen (*239*), and for respirating gases (*114*).

MEASUREMENT

Gravimetry. A number of direct-reading balances and semimicrobalances, some using illuminated ground-glass scales, are now available commercially (*158*, *327*, *352*, *364*). One model (*364*) has a weight dial and levers outside the case for remote control of all weights to avoid touching them. A vernier-type scale on a Chain-o-matic balance is also used (*453*). Deryagin (*118*) has been able simultaneously to increase the sensitivity of a balance and shorten its period of oscillation by means of photoelectrically detecting the displacement of the balance needle from its null position. The current thus produced flows through a coil magnet to restore the balance to its equilibrium position. A similar setup using a Thermocap relay, which detects any motion of the balance beam without direct contact and returns the balance to equilibrium through a servo-system controlling a chain hanging on one end of the beam, has been reviewed by Müller (*328*). The same discussion cites the general need for automatically recording balances for a wide variety of uses and the various methods which may be used. A radioactive electronic detector can give a microbalance a sensitivity of at least 1 microgram per mm. deflection on a galvanometer (*154*).

Duval and co-workers have continued their work with the photographic recording thermobalance (*127–133, 135, 137–139*). Suitable temperatures have been given for heating a large number of compounds as well as data on the burning of a filter paper (*134*) and the pyrolysis of asbestos (*136*). Brefort (*41*) has described a thermobalance which records continuously by means of a photoelectric cell either at a constant temperature or during a definite temperature schedule.

Special uses of recording balances for adsorption curves (*150*), for moisture loss (*424*), and for sedimentation rates (*419*) have been described. Extensive foreign adaptation of torsion balances for measuring surface tension is indicated in Picon's description of a pen-recording absolute tensiometer (*371*); Andersson and co-workers' photographic-recording surface balance (*10*) is another example. Pouradier and Dubois have fitted a dipping-plate tensiometer with a recording device (*376*). The plate is maintained in equilibrium by a force exerted by an electromagnetic balance, and the current required to do so constitutes a measure of the surface tension.

Volumetry. Measurement of the volume of the desired constituent appears to be a fairly common basis for certain types of automatic analysis. A number of devices and techniques have been described, including two Russian instruments, one a gas analyzer of the Orsat type (*244*) and the other a gasometer (*19*) used to record the gas collected at constant pressure from a chemical reaction (such as hydrogenation, or dissolution of iron in hydrochloric acid). The constancy in pressure is attained by connecting the gasometer with a constant liquid level vessel where addition or removal of the liquid is handled by a small motor controlled by three contacts sealed into a mercury manometer. A commercially available semiautomatic carbon determinator eliminates hand operation of the traditional leveling bottle by raising and lowering all solutions by oxygen pressure (*276*).

Measurement of oxygen consumed in the oxidation of oils is the basis of an automatic apparatus mentioned in a paper on the laboratory evaluation of oil deterioration (*281*). The oxidation of fats has been studied automatically by two devices. One (*311*) was built for the volumetric determination of oxygen absorption by fats at elevated temperatures and constant pressures and records by a pen float on mercury. The second is a new apparatus (*310*) which replaces the oxygen absorbed by means of a copper (II) sulfate electrolytic cell electrically connected to an identical cell evolving the same amount of oxygen into a volumetric column. For physiological work, an apparatus (*309*) has been developed to measure the beat volume of the heart, involving continuously recording oxygen consumption.

Constant volume pumps have been described by Sheen (*315, 405, 406*) as being particularly useful in automatic titration systems (see Titrimetry section). A typical constant-rate reagent-feeding device has been described recently (*361*). So-called automatic pipets are much used in biochemical methods (*351*). One type (*161*) delivers as many as 20 or 30 samples per minute in quantities up to 2.0 ml. by pressing a plunger, thus eliminating the use of the mouth. Another type (*138*), also on the market, exposes only glass and mercury to the liquid and controls the flow by means of a double glass valve with an iron core. A current passes through a solenoid coil which opens the lower valve while closing the upper one. A solution flows in the upper valve, displacing mercury until the current shuts off. Tests on a 1-ml. model showed delivery at 4-second intervals with maximum deviations of 0.004 ml.

Volume changes of solids continue to form the basis of relative humidity measurements. Both the hair and membrane types are advertised (*170, 195*). Another volumetric measurement of a solid is made by a recording dilatometer (*442*) for measuring thermal expansion. The record is made by a recording potentiometer which prints the strain-gage output directly, as well as the temperature of the sample.

Densimetry. Although one of the more nonspecific of all physical properties, density can in special situations give considerable analytical information, and consequently its measurement, at least for liquids, has been widely automatized. Munch (*335*) mentions that, although various methods have been used, there is considerable room for improvement.

Recent work and commercialization of continuous densimeters have centered mainly on one of two methods.

One of these uses the classical Archimedes approach by using floats or plummets. The main variation lies in the means of measuring the height of the float. One industrial model (*335, 380*) has chains hanging on the floating plummet similar to the arrangement of chainomatic balances. As the density changes, it rises or falls to establish equilibrium and give a measure of the density through its vertical position. An iron core can be included in the float's construction, and an inductance bridge circuit can be used in recording its travel up and down. Temperature compensation is available automatically or manually, and various models for different pressures are available. A patent (*463*) describes a densimeter for continuously recording the density of metallurgical pulp flowing from a classifier. The two floats in it have different buoyancies and are connected to a balance beam and a stationary measuring device. The beams are displaced different amounts for changes in the density of the fluid. A similar idea in another patent (*306*) has two identical floats connected by a system of levers so that, when one float is immersed in the sample liquid and the other in a reference solution, a difference in the two densities results in a displacement of a shaft holding a pen which records the motion in a clock-driven chart.

The second general method of attack on the problem of automatic densimeters consists in placing two dip tubes at two different levels in a tank of the liquid (*55, 325, 326*). Air or an inert gas is caused to flow at a constant rate through these two dip tubes. The magnitude of the differential pressure is a function of the difference in depths and of the specific gravity. One method (*325*) of measuring this pressure differential depends on a pneumatic null-balance system. Another (*55*) uses a differential bell-type meter, with mercury in the meter body indicating the pressure differential, its height being electrically transmitted by means of an inductance bridge.

Denyes and Fox (*116*) have detailed the use of the differential pressure method in the continuous and accurate specific gravity measurement of a viscose spinning bath. Further applications in the automatic density control of sirups have also been described (*308, 414*).

Manometry. When manometric methods are used to measure the desired constituent, automatic recording of the pressure involved is frequently possible.

A number of portable gas analyzers for carbon dioxide and for oxygen have appeared on the market recently (*15, 16, 195*), which operate by drawing a definite volume of the gas sample into a closed system. The gas is then caused to pass through a material which absorbs the desired constituent (either carbon dioxide or oxygen), and the resulting decrease in pressure of the constant-volume system is indicated. If the sorbent is liquid, the liquid itself may serve as the manometer fluid whose height is calibrated directly in per cent. When the sorbent is solid the pressure may be indicated on a needle gage, also calibrated in per cent units.

Continuous gas analyzers based on manometric measurement of the sample with and without absorption of the desired constituent have been developed by Guillemin (*199*) and by Guy (*202*). Both use a hydrodynamic resistance bridge analogous to a Wheatstone bridge, with a differential pressure indicator replacing the galvanometer between the arms. A major advantage lies in the differential nature of the pressure measurement, since changes in total incoming pressure to both sides do not affect the results. The substitution of the differential pressure-measuring element for the two meters required in other before-and-after-sorption manometric analyzers enables simpler design and greater sensitivity. A very sensitive differential manometer (*307*) detecting pressure differences as little as 10^{-6} atmosphere over a range of 1 mm. of mercury to 1 atmosphere, developed at the National Bureau of Standards, is based on the principle of an aneroid barometer. The actual measurement is of the separation of a pair of nesting diaphragms indicated by an unbonded wire-resistance displacement gage. The two diaphragms are soldered together to form a very thin capsule which contains the gas or vapor, the other vapor surrounding the capsule externally. One diaphragm is stationary, while the other is attached to the displacement gage, whose four resistance wires are arranged in a Wheatstone bridge. Movement of the diaphragm lengthens one pair of the wires and shortens the other pair.

A very sensitive means for measuring pressures from 10^{-3} to 10 mm. of mercury is available in a radioactivity vacuum gage (*438*). Variations in pressure cause changes in the number of ions formed per unit of path length by each particle emitted from a source of radioactivity.

Mercury manometers have been used in a number of automatic devices for various applications. One (*95*) is used to indicate the quantity of distillate in the receiver of a Podbielniak still used for the low temperature fractionation of C_1 to C_5 hydrocarbons. The volume and temperature of the closed distilling column and receivers and connecting piping are kept constant. Thus the height of the mercury manometer, as measured and recorded by an electrically driven probe, is a direct indication of the quantity of the vaporous distillate.

An unusual transmitting manometer (*421*) used for micro oxygen-uptake experiments has fine platinum filaments stretched centrally in each limb, which form part of a Wheatstone bridge. Pressure changes alter the effective lengths of the resistances, which are indicated on a galvanometer.

Watson (*460*) has patented a hydrogen meter for flowing gaseous mixtures which measures the pressure of the hydrogen that passes through a permeable palladium sleeve.

A commercial vacuum moisture recorder (*71*) measures the water content of moving sheets (paper, cellulose, cotton, and textiles). The instrument consists of a pickup cell (placed close to the surface of the material), a vacuum pump, and a motor. As the material moves along, a small part of the air immediately adjacent to, and in equilibrium with, the moisture in the material is drawn through the meter. Calibrations are available for various ranges.

Specific gravity of liquids is measured manometrically in two devices recently described. One (*117*) depends on the pressure difference between two dip tubes through which a constant flow of air is purged into the sample; and the other (*304*) employs an open-top float containing mercury through which air is bubbled. The resistance to the air stream depends on the vertical position of the float, which in turn is determined by the density of the liquid floating it. The effective moisture concentration in soil can be measured by its capillary tension (*374*, *375*). A special tensiometer is used with a cup buried in the soil and provided with a gage marked in inches vacuum. Automatic watering in greenhouses is effected by having the device operate an electrical contact which adds water to the bench when it is needed.

Viscometry. The use of viscosity measurement in automatic methods of analysis is definitely increasing. Trends in this field appear to consist mainly of improvements and refinements in techniques and design, and of detailed studies on feasible applications. A series of papers on rheological methods of control for the pharmaceutical, cosmetical, milling and baking, and paint industries has appeared recently (*9*, *32*, *305*, *474*), all predicting much wider use.

The major method for determining the viscosity of a liquid, appearing in the current literature, is based on the torque exerted on a rotating stirrer. A wide variety for special and for general purposes is available commercially. Most of these involve a rotating paddle, spindle, or disk (*44*, *52*, *54*, *266*, *282*, *321*, *387*, *465*). Features include auxiliary differently shaped spindles and cups (*47*, *160*, *321*), temperature recording and/or control (*52*, *160*, *377*, *387*, *415*), replaceable torque springs (*195*), ease in cleaning, and stroboscopic timing control (*266*). Applications include anesthetic gases (*210*), cellulose fiber suspensions (*253*), thixotropic gels or polymerizing substances (*195*), size in papermaking (*321*), petroleum (*387*), asphalt (*377*), clays and shales (*415*), paints (*266*), motor oils (*171*), and thick liquids and plastics (*112*).

Rotational viscometers in which the sample cup, rather than a stirring element, rotates are also finding extensive use (*160*, *192*, *377*), as is the float method (*112*, *120*, *122*, *171*).

A number of viscometers are based on the Poiseuille equation and determine the viscosity by the pressure drop across a tube of given dimensions with the fluid flow kept constant (*439*) or by the pressure required to maintain a constant flow (*60*).

Magnetometry. The high paramagnetism of oxygen in contrast to most other gases is being exploited extensively in oxygen analyzers, and new techniques and applications are constantly being reported. Most of these (*222*, *260*, *287*, *383*, *456*) do not differ significantly from those reviewed last year. Several, however, involve interesting new measuring elements for increased sensitivity and rapidity of response. Some of these include pressure measurement by a flexible membrane capacitor (*301*), induced voltage in a rotating slotted disk (*234*), and angular rotation of a special conduit (*347*).

A magnetic comparator for comparing small fabricated ferrous parts with a standard to determine differences in composition and other characteristics is available commercially (*179*).

Thermometry. Temperature is the measured physical property in a wide variety of automatic methods. Only those in which the temperature is the most significant item of data obtained in the analysis, however, are classified under this section. Other methods, using temperature measurement as a more or less subsidiary item, are considered separately (see Calorimetry and Thermoconductometry). Thus this section includes such items as certain colligative properties, freezing and melting points, and others in general not involving heat of reaction or heat conductivity.

The old reliable wet- and dry-bulb temperature method for humidity measurement still receives considerable attention. A wide range of indicating devices is available all the way from the "pocket humidicator" (*467*) to recording or indicating hygrometers (*398*, *430*). This general idea has been adapted to the moisture testing of dry materials (*119*), in which the relative humidity of the atmosphere surrounding the sample is assumed dependent on the water content of the sample itself. Different salt solutions are used on the wet-bulb side for various moisture levels.

Stock and Fill (*422*) have built a melting point indicating device in which a fine glass rod rests on the sample in the melting point tube and carries a light platinum bridge at its upper end. The material melts, the rod sinks, and the platinum makes electrical contact with a pair of mercury cups to cause a buzzer to sound. Presumably the temperature at this point could be automatically recorded. A fundamentally similar device for automatic determination of the aniline points (*48*) of petroleum products involves photoelectric detection of the clearing of the clouded solution which occurs at the aniline point temperature. In this case a light bulb flashes when the equilibrium point is reached, and a relay system controls the heating or cooling. Automatic freezing point determinations have been described in two foreign papers (*109*, *224*).

Collins has patented an apparatus (*91*) for rapid and continuous measurement of the carbonaceous deposit collecting on catalysts used in cracking, reforming, or hydrogenating, which essentially imposes a high frequency (about 15 mc.) alternating current across an insulated conduit through which the sample flows at a constant rate. The temperature difference before and after exposure to the high frequency gives a correlation (through a calibration curve made with knowns) with the amount of carbonaceous matter present. Automatic thermal analysis involving recording the differential temperature between the sample and some reference material (*197*, *454*) and the rate of cooling with time (*370*) has been described. Greenhill and Whitehead (*194*) developed an apparatus for measuring and recording small (0.01°) temperature changes in liquids, especially useful for determining heats of wetting and adsorption of fine powders in liquids.

Stack has reviewed (*418*) applications of the General Electric dew point recorder and emphasized the increasing importance in industry of accuracy and convenience of such determinations.

Wearne (*461*) describes the successful use of a very simple warning method for changes in gas quality, involving the use of a Bunsen flame, in the cool blue zone of which a thermocouple is located. When the flame shortens, the thermocouple tip is heated and an alarm is sounded.

Calorimetry. This class of methods includes measurement of temperature changes resulting from some chemical reaction of the sample or detecting element. Catalytic combustion with oxygen forms the basis of most of these, although some have been described involving heat of decomposition and of dissolution or absorption.

Examples include three (*38*, *229*, *250*) for the determination of oxygen in a flowing gas when a constant excess amount of a vaporous fuel (usually methanol) is added, and Wheatstone bridge measurement of the resulting temperature increase is made. Successful application of an analyzer of this type has been described for the automatic control of total combustion air for a process heater (*38*). Fuel consumption was reduced an average of 15%.

Combustible gases may be measured in much the same way. One company (*317*) advertises a wide variety of recorders and portable instruments for explosive and combustible gases and vapors, including special designs for benzene, carbon monoxide, and methane. Two Belgian patents (*381*) describe a detector in which the exothermic heat of combustion causes the deformation of a deformable member which actuates an indicator. Lindsley and Yoe (*291*) and Vylomov (*457*) determine carbon monoxide by this method, the former by oxidation over hopcalite and the latter over a hopcalite–silica gel mixture, following removal of the heavy hydrocarbons by activated carbon and of moisture by silica gel or alumina gel. A commercial combustibles recorder (*17*) measures the heat of combustion on a catalyst filament by means of an alternating current potentiometer.

Huguenard (*237*) has a method depending on a platinum wire heated to 1200° to 1300°, which causes exothermic reactions of carbon monoxide, hydrogen sulfide, hydrogen, ammonia, alcohol, ether, and illuminating gas and causes endothermic dissociation of carbon dioxide, water, and carbon tetrachloride. According to him, the nature of a foreign gas or of a mixture can be determined from its behavior on a platinum wire when heated to various temperatures. Another analyzer designed specifically for ammonia-air mixtures (*445*) measures the ammonia content by the rise in temperature of a platinum wire at about 200°. It is said to be independent of the rate of flow.

The heat of hydration when water is absorbed—e.g., the Dewcel, in which a resistance bulb covered by a lithium chloride-impregnated wick is used (*479*), or other dehydrating agents such as magnesium perchlorate (*241*)—has found extensive application in paper mills.

Titrimetry. Stoichiometric chemical reactions involving addition of a reagent of known concentration to the sample until an end point is reached at which a pronounced physical property-change takes place are increasingly being performed automatically.

A number of potentiometric titrators have been described (*200*, *201*), including one (*189*) especially designed for control of milk quality. Some plot the potential against time or amount of titrant added (*254*, *379*), while a recently commercialized model (*23*, *344*) conducts the titration, by electrically operated valves on a standard buret, to a previously established pH or millivolt potential and stops, whereupon the operator reads the meniscus. An accuracy up to 0.1% is claimed and routine titrations can be run in as little as 1.5 minutes. Its sturdy construction has been confirmed in use on ships at sea. A syringe-buret is used in an automatic conductometric titrator (*252*) and can dispense as much as 10 ml. with an accuracy of 0.001 ml. (limited by temperature constancy).

Lingane in a review of developments in electroanalytical chemistry (*294*) discusses automatic titrimetry. Sheen (*336*, *405*, *406*) has described automatic titration systems using controlled volume pumps. The sample is measured on one side of a duplex pump and the amount of titrant necessary to maintain the resulting mixture at the end point is measured in on the other side. Thus the ratio of the two flows provides a continuous measure of the desired constituent. It can be used in pH, redox, conductivity, color, turbidity, or specific gravity titrations. Each application must be studied to determine the control point to be measured according to the slope of the titration curve and desired buffering action, as well as the optimum method of end-point measurement. This method requires in practice about 1 quart to 2 gallons per hour of standard titrant. Another similar setup (*396*) for continuous titration of the output from a flowing-stirred reactor has been found useful in studying reaction rates.

Titrations where the titrant is added by electrolytic generation, as described last year, are continuing to be developed (*336*). A commercial apparatus, the Titrilog, has been placed on the market for continuously recording trace quantities of sulfur compounds (*13*, *14*, *98*). Compounds which can be titrated using electrolytic bromine include sulfur dioxide, hydrogen sulfide, mercaptans, thioethers, thiophenes, and disulfides. The apparatus has found use in the odor control of natural gas. An important feature is the filter solution, automatically placed in the system every 15 minutes, which enables determination of hydrogen sulfide and sulfur dioxide separately, when they are both present in very small concentrations. A portable model for field use needing only electric power is also available (*100*).

Chronometry. Only two significant methods involving the measurement of time have appeared. These are both commercially available, biological assay units which measure the circles of inhibition in biologic cultures. One of these (*475*) is operated by placing the dish to be measured in a holder, depressing a foot pedal, and recording the circle diameters as they appear in illuminated numbers. It will handle a rate of about four dishes per minute, each dish containing six circles, resulting in 24 readings per minute. The chronometric time measurement enters in as a result of rotating the dishes at constant speed, and a photoelectric unit actuates the timing device. The other commercially available unit (*1*) also involves placing the Petri dishes in the scanner head and depressing the starter switch. It handles the scanning, computing, and recording operations continuously at a rate of 240 dishes per hour, reading to an accuracy of 0.1 mm. One model prints the average diameter of each group together with a serial number of each dish; another model records the data in strength units as derived from the ratio of the average diameters of known and unknown; a third model records similar data, but also automatically rejects results from plates having deviations from the average greater than 2 mm.

Sonimetry. Two gas analyzers have been recently described, which make use of the passage of sound waves through the sample. Hubbard (*235*) discusses four types of equipment applicable to gas analysis, as well as regulation and control. All are based on the properties of the piezoelectric resonator which is stable and highly selective. Faulconer and Ridley (*153*) emphasize the necessity of continuous analysis of mixtures of oxygen, nitrous oxide, ether, and nitrogen in anesthetic work. They found that the spread of the sound velocities in three of these gases is large enough to permit analysis based on this property. With the addition of a magnetic oxygen analyzer, nitrogen also may be determined automatically (by difference from the sonimetric results for oxygen and nitrogen together). Basically, the gas sample cell has two transducers which measure the time interval for a sound impulse to travel from one end to the other and through an amplifier back to the first end. The frequency at which the circuit used oscillates is thus a function of the substance present in the cell and this frequency is measured electronically. The apparatus, as designed for a two-component system, is simple enough, but to determine a mixture of three requires a much more complicated apparatus involving absorption of the ether with sulfuric acid.

Emissimetry. Extensive work in the field of automatic determination of metals by measurement of spectral line intensities has been reported. Nachtrieb's book (*341*) has a brief chapter on direct-reading spectrometers and includes a discussion on two types of detectors, Geiger-Müller counters and electron multiplier phototubes. The Harrison, Lord, and Loofbourow book (*211*) mentions detectors and direct-reading spectrometers and also describes the Harrison automatic comparator for line intensities from photographic plates. Other literature references describe photoelectric spectrographic analysis (*64, 277, 346*), including instruments designed for both photographic and photoelectric measurement (*90, 357*).

Recent developments on the Quantometer have been described by several authors (*11, 78, 218, 220, 286*). Features include improved thermal and mechanical stability and an automatic circuit to compensate for zero drifts always present in direct current amplifiers. Successful applications have been claimed for silicon, magnesium, copper, nickel, iron, and manganese in aluminum alloys (*66*), the same elements plus chromium, molybdenum, aluminum, and tin in steel (*72*), phosphorus and copper in steel (*219*), stainless and tool steels covering wide ranges of composition (*215*), 18–8 stainless steels (*217*), low-alloy (*216*), and high-alloy (*214*) steels, and results of more than 2 years' experience in roller bearing steels (*448*).

A Geiger-counter spectrometer for x-ray fluorescence analysis has been described (*173*) for measuring the *K* series of lines of elements 22 to 50. The method is applicable to materials in any physical state: bulk solid, powder, liquid, or gas.

Determination of lead in air with extreme sensitivity can be accomplished by radiant energy emission at 2203.5 A. Here again, the Geiger counter has proved its usefulness (*12, 270*).

Absorptiometry. The absorption of radiant energy by gases, solids, or liquids has been mentioned as a basis for automatic analysis more often than any other physical phenomena. That such measurements are nondestructive to the sample and practically instantaneous in response seems the most likely reason for this. Absorptiometric methods are considered according to wave-length regions: infrared, visible, ultraviolet, and x-ray. Those included are restricted mainly to continuous measurement of flowing streams, rather than automatic recording of absorption spectra of single samples.

Infrared Region. Advances in this field have been made both in instruments and in applications. Kivenson (*263*) has reviewed considerations in the design of double-beam analyzers, including descriptions of various optical and electronic arrangements. White *et al.* (*470*) describe the adaptation of a recording infrared spectrometer for use in continuous determination of six different components in a flowing sample stream. In it the percentage absorbed at each of six different wave lengths is automatically recorded. Chapman and Torley (*76*) use a mobile setup of a commercial instrument which can spot-check the concentration of several components or make a continuous record of a single component. Elliott (*144*) describes a positive filter-type infrared gas analyzer utilizing a jet-vane system in conjunction with a photoelectric cell for detecting the pressure unbalance between two positive filter detector cells. This differs from the German methods using a microphone condenser system. The working model was constructed for preliminary tests in carbon dioxide determination.

Coggeshall and Muskat (*89*) patented an automatic system of process control by infrared spectroscopy, in which values are obtained at various wave lengths by means of a program device to readjust the monochrometer. The signals are then electronically added and solutions to simultaneous equations yield the concentration values of each constituent. If the system is essentially binary, the quotient of two signals may be used to control a process parameter. Another patent by Ritzmann (*390*) improved this instrument by the use of a separate monochromator for each wave length.

The Luft apparatus (*300*) using the Pfund and Gemmill principle (*365*) has been described by Hindley (*228*) and made available commercially (*319*). The commercial model is designed for silver chloride (or other materials) cells 0.1 to 9.0 inches long. Detection involves the difference in pressure caused by the two beams (sample and compensation) in two chambers separated by a diaphragm which vibrates to generate an electric signal (as a microphone). Gases usually analyzed are in the 3 to 300 p.p.m. range and a list of 24 toxic materials which can be measured is given (*319*).

Pneumatic autodetection for infrared gas analysis has been described by Miller and Russell (*314*). After a review of various possible methods of infrared detection, they chose a differential manometric pressure device, consisting simply of a drop of fluid in a capillary. A photoelectric position indicator was used in which the drop acted as a cylindrical lens to focus light on a slit behind the capillary onto one of two photocells which are arms of a Wheatstone bridge. The apparatus can detect changes of 9 p.p.m. of carbon dioxide in air containing about 300 p.p.m.

Numerous other papers have appeared describing successful applications and techniques in the field of automatic infrared analysis: complex gas mixtures under varying plant conditions (*175*), mixtures of air and gas in the open-hearth furnace (*92*), carbon dioxide in respiration studies (*33, 168*), carbon monoxide and carbon dioxide in pilot plant and refinery operations (*413*), petroleum gas streams (*207*), total unsaturation in a furfural extractive distillation column separating *n*-butane and 2-butenes (*469*), sequential determination of 18 plant streams for methane (*469*), ethylene oxide in pilot plant facilities (*213*), organic solutions (*113*), impurities in a GR-S synthetic rubber plant stream (*265*), and continuous measurement of the beat volume of the heart (infrared absorption of the blood) (*309*).

Visible Region. The greatest activity in this field has been in the determination of gases in gaseous or liquid samples. Continued progress in the use of the oxyhemograph and similar devices for oxygen in blood has been reported (*188, 212, 262, 446*). It has been stated (*302*) that this apparatus should be part of the routine medical equipment in every operating room where prolonged operations are being undertaken. This device has also been placed on the lobes of aviators' ears inside the helmet so that, when the oxygen content of his blood decreased dangerously, a red light would flash on the instrument panel. Kalmus and Sanders (*255*) have designed an unusual densitometer which has been used as a hemoglobinometer. It has high stability, and full meter deflection can be obtained with a light flux of only 0.5 microlumen. The determination of oxygen in gases has been handled colorimetrically by decolorization of sodium anthrahydroquinone-β-sulfonate (*39*), by indigo carmine (*303*), and by nitrous oxide (*209*). Measurement of the radiant energy absorbed by nitrogen dioxide is described as the basis of its determination in air (*248*, *269*) and for a kinetics study of the reaction between nitrogen pentoxide and nitrous oxide (*411*). Greater sensitivity is obtained by absorbing the nitrogen dioxide in dilute sulfuric acid and measuring the resultant color (*269*). Dudden (*126*) determines nitric oxide in coal gas by electrolytic oxidation to nitrogen peroxide, which then develops a color in Griess reagent.

The photoelectric determination of atmospheric sulfur dioxide (*257*) in smelter areas, where hydrogen sulfide is not present depends on the blue color formed with dilute starch-iodide solutions. A Russian automatic device (*391*) for signaling the presence of gases in air passes the air through a pyrolysis chamber and then around a transparent "indicating film." Light passing through this film and onto a photocell actuates a recorder. Application is described for bromine and ethyl chloride in small amounts.

Hawes *et al.* (*221*) have described the use of a commercially available flow colorimeter for determination of chlorine or chlorine dioxide in plant streams. This double-beam instrument can determine any material absorbing in the wave-length range of 350 to 950 mμ. A residual chlorine analyzer (*191*) based on the *o*-tolidine color has been described in detail.

An "alcometer" based on Greenberg's (*193*) colorimetric determination of the alcohol in blood has been recently marketed (*2*). The alcohol reacts with iodine pentoxide to produce free iodine, which then reacts with starch-iodide solution. The scale is calibrated directly in per cent alcohol in the suspect's blood.

A continuously recording colorimeter has been used by Chaney (*74*) to determine protein-bound iodine in blood. Here the catalytic action of iodide on the reduction of cerate by arsenite is measured. A straight line may be obtained, whose slope depends on the iodine concentration. Other applications include any reactions where color changes occur. It would be useful, for example, for automatically measuring the time required for full color development. The method for iodine has a sensitivity of 0.0002 mg. per ml. of final solution.

Two Russian authors (*80*) measure the concentrations of two liquids being mixed by previously adding a dye to one of them and comparing the resultant color dilution.

Absorption of light passing through paper chromatograms as measured by photomultiplier tubes forms the basis of a system of automatic recording paper chromatography described by Müller and Clegg (*332*). A similar type of scanning instrument for amino acids was described by Fosdick and Blackwell (*167*). Levy *et al.* (*288*) have designed a recording polarimeter where the operator is replaced by a photomultiplier tube. An alternating current proportional to the unbalance between the two halves of the field actuates a servo-mechanism to rotate the analyzer to produce optical balance. The recorder indicates the angular travel of the analyzer.

A new type of radiant energy detector called the phototransistor (*8*) is about the size of a rifle bullet. Its ruggedness and simplicity should induce its future use in automatic absorptiometers. It is similar to the recently developed germanium transistor, except that the output current is controlled by light rather than by the current of the emitter probe (*142*).

Ultraviolet Region. The absorption of ultraviolet radiant energy has not been found as widely useful as has that of the infrared and visible regions, but it has solved some special problems. One instrument manufacturer (*57*) has made available an ultraviolet spectrophotometer for providing continuous automatic analysis of process streams. It can also give periodic analysis of as many as three process streams with one instrument and features automatic standardization at intervals to compensate changes in the various factors influencing the absorption. Kivenson (*263*) has considered the design and features of both infrared and ultraviolet double-beam analyzers, and, together with co-workers (*264*), has also described the details of an ultraviolet analyzer for determining the amount of styrene in a styrene-butadiene feed stream.

Glasser (*187*) notes that only a few instruments are commercially available for continuous analysis and predicts that widespread use of such ultraviolet analyzers will not come until certain difficult problems are solved. Essentially these concern the age-old problem of interference by substances other than the desired constituent and the difficulty of combining sensitivity to small radiant energy absorption with long- and short-time stability.

Two patents recently were issued describing instruments for various gases in air (*205*) and for diolefin mixtures (*392*).

X-Ray Region. Absorptiometry in the x-ray region is still largely restricted to single samples. However, the progress being made in the automatic recording of x-ray absorption spectra offers hope that the x-ray photometer may soon develop into an accepted analytical automaton in the true sense of the word. The further development of this type of method to measure continuously changing concentrations is possible for some applications, such as tetraethyllead in gasoline, sulfur in petroleum products, and halogens in plastics (*65*, *483*). Liebhafsky (*289*) expresses the hope that x-ray absorptiometry may be useful in evaluating the quality of crushed minerals on a moving conveyer belt, as well as in direct control in operations involving lead, sulfur, and halogens as mentioned above. An x-ray photometer (*184*) designed for the tetraethyllead problem can also be used for odor control of natural gas (when sulfur compounds, such as the mercaptans, are responsible for the odor).

Thermoconductometry. The thermoconductometric method of analysis has been found useful for a multitude of gases in a wide variety of studies. At least ten different companies advertise gas analyzers depending on this type of measurement. The literature available from most of these manufacturers provides a wealth of descriptive material on construction details and suggested applications (*18*, *56*, *67–69*, *111*, *147*, *148*, *183*, *190*, *222*, *450*). In addition to the traditional carbon dioxide recorders, commercial models are available for the following gases and vapors: ammonia, argon, benzene, carbon monoxide, chlorine, ethanol, helium, hydrogen, methane, methanol, nitrogen, nitrous oxide, oxygen, sulfur dioxide, and water vapor.

One gas analyzer-recorder (*69*) is especially designed to measure simultaneously oxygen, carbon dioxide, and carbon monoxide.

> A continuously flowing sample is drawn by water aspiration and split into two parts, one going through a channel to which hydrogen is added continuously from an electrolytic generator. This goes through the reference side of the oxygen cell, then through an electric furnace where water is formed, and back through the sample side of the oxygen cell. The loss in hydrogen represents the oxygen originally present. The second portion goes through the sample side of the carbon dioxide analyzer first, then through an absorber, and back to the reference side of the same cell to provide a measure of the carbon dioxide present. This same stream then receives a continuous supply of oxygen from the electrolytic generator to convert carbon monoxide to carbon dioxide, and is then analyzed for carbon dioxide in the same way as was the original carbon dioxide.

Recent patents issued for thermal conductivity analyzers include an Italian one (*436*) for carbon monoxide, where the oxidation is catalyzed by cuprous oxide, and three in this country (*88*, *238*, *480*). One of these (*88*) features an automatic compensating device for suppressing pressure variations at total pressures less than 100 mm. of mercury.

Recent special applications of automatic thermoconductometry include the determination of carbon dioxide in alveolar air (*383*), hydrogen in chlorine (*108*), water vapor in air (*81*), studies of adsorption (*102*), and investigations of the exhaust gases of combustion engines (*26*).

An interesting field of application is the determination of dissolved oxygen and dissolved hydrogen in water (*68, 176, 247*). Oxygen is scrubbed from the sample by hydrogen and the thermal conductivity is compared before and after combustion to water vapor. The recorder reads in parts per million of dissolved oxygen with a full scale range of 0 to 0.2 p.p.m. The technique for hydrogen—e.g., that generated from corrosive dissociation of boiler water—is similar, except that the range is 0 to 20 parts per billion of hydrogen.

Turbidimetry. Two general types of analysis lend themselves well to the continuous determination of turbidity. One is the measurement of smoke density in the curbing of atmospheric pollution. Many instruments for doing this type of measurement have become available and differ little fundamentally among themselves (*181, 261, 286, 368, 369, 385, 440*). The other general type involves the formation of a fog as the basis of the determination of sulfur trioxide (*4*) and of halogenated hydrocarbons or carbon disulfide (*20*). A recording turbidimeter for water purification plants has recently been placed on the market (*182*). It is a ratio-measuring instrument, since the ratio of scattered light to transmitted light is assumed to be proportional to the turbidity of a liquid. The ratio measuring feature, of course, cancels out variations in color or source intensity.

Refractometry. Munch (*335*) has made the remarkable statement that measurement of refractive index is second only to that of density for continuously indicating the composition of mixtures. Only recently, however, has a continuous-flow refractometer become commercially available (*378, 379*). This expensive instrument, developed by Barstow (*21*), is essentially an immersion refractometer with the usual optics producing the familiar light-dark field which is observed by a photomultiplier rather than the observer's eye. A range of about 1.33 to 1.54 is covered to within 3 parts in the fifth decimal place on clear samples. Applications include styrene, petroleum products in cracking plants, fractionation column products, vinylidine chlorides, and glycol.

Two papers (*432, 481*) describe instruments embodying improvements on Claesson's apparatus. Pen and ink recording is preferred over Claesson's and Svensson's photographic methods (*223, 425, 426*), although the latter two have built apparatus which gave simultaneous records of both the refractive index and its derivative.

Jones *et al.* (*251*) have described a continuous recording refractometer for industrial control of both opaque and clear liquids, which is based on the intensity of internal reflection near the critical angle in a prism in contact with the flowing sample stream.

A recent announcement (*31, 141*) has been made of a recording microwave refractometer developed by Birnbaum at the National Bureau of Standards. It can be used for continuous monitoring of impurities in gases or liquids and can be adjusted over a wide band of microwave frequencies for measurement of dielectric constants.

Diffractometry. X-ray diffraction techniques seem still to be limited to single samples. The advances made in using recording x-ray spectrometers, nevertheless, deserve mention (*259, 268*). One modified recording instrument (*83*) permits the direct comparison of the diffraction patterns of two separate powder samples. Applications of x-ray spectrometers to process control have been described by Considine and Eckman (*94*).

A gas analyzer which might be considered a type of diffractometer has been recently patented by Hillier (*227*). The component parts are analogous to those of a mass spectrometer, but the procedure is to impinge a stream of electrons upon a gaseous sample and then measure the velocity distribution. The electrons emerge with a wide range of reduced velocities depending, for any one electron, on the nature of the collisions and on the probability of such collisions occurring. These electrons are then subjected to an electromagnetic (or electrostatic) field which bends the path of each electron an amount depending on its particular velocity. By regulating the strength of the deflecting field, an energy distribution pattern may be recorded by a standard potentiometer recording the output of an electron multiplier tube (a standard photomultiplier tube with the photosensitive cathode removed). The data obtained fundamentally offer information on the possible energy losses which an electron can suffer in an inelastic collision with a gas molecule, as well as the relative probability of occurrence of such a collision. This probability, of course, in turn depends on the number of gas molecules present. When the collision involves severing a chemical bond by the electron, its resultant loss in energy will depend on the bond strength and type, so that information on structure can be thus obtained.

Reflectometry. The reflection of light by opaque surfaces can be used to evaluate various materials. Von Brand (*455*), for example, has described applications of a portable continuous smoke recorder. A continuous stream of air is drawn through a filter paper tape which collects the smoke particles. A photoelectric recorder then measures the reflectance of the stain produced on the moving strip. There have become commercially available recently (*318*) a number of portable devices in which the gaseous sample is passed through a glass tube containing a granular substance. This substance changes color in proportion to the amount of the desired constituent passed through. Models are available for carbon monoxide or hydrogen sulfide.

Müller and Clegg (*333*) have used reflectance measurements in some of their automatic paper chromatography work.

A recently marketed automatic hydrogen sulfide analyzer (*335*) covering a range of 2 to 500 p.p.m. will determine that gas in natural gas, carbon monoxide, hydrogen, and the inert gases. It now uses a strip of cloth impregnated with lead acetate, which is advanced to expose an unused section at the end of each test period.

A recording turbidimeter (*182*) (see Turbidimetry section) actually measures the light reflected by the particles in the solution.

Nickerson *et al.* (*345*) have designed an automatic colorimeter for cotton, which has been commercialized (*178*). The instrument provides for automatic inspection of the reflectance of raw cotton for the purpose of grading. It gives direct readings of yellowness based on the Hunter coordinates (which can be converted to Munsell values). The present instrument is limited to the range of cotton colors showing graphically on a two-dimension scale simultaneous values for reflectance and yellowness, but it can be adapted to other limited ranges of color, in either two or three dimensions.

The instrument has a 6-volt spotlight source with aluminum mirrors diverting beams onto the sample surface at 45° angles from opposite sides. There are five barrier-layer cells: One monitors the light source, one views the test area perpendicularly through a green filter to provide the reflectance current, and the other three, connected in parallel, also view the sample perpendicularly, two through blue filters, and the third through a green filter with the cells' polarity reversed. These three then provide in combination a residual yellowness current which is proportional to the reflectance difference between the blue and yellow-green portions of the spectrum.

Conductometry. Electrical conductivity measurement of liquids and solids is increasingly used as a basis of automatic analysis and control. The recent literature on the subject has described successful applications and refinements in the design of equipment (*50, 243, 393*).

Conductivity is used mainly for one of two purposes: to determine water in solids or to determine ionized substances in water. The available moisture content of soils is of ten conveniently determined conductometrically (*36, 164*). Measurement of the water in moving sheets of paper using the Moist-O-Graph continues to be handled by this method (*3, 51, 340, 407*). The conductivity of water-sorption films has been used for the measurement of humidity, and various applications of this technique have been described (*5, 6, 8, 165, 226, 462*).

When it is desired to measure ionic substances (gases or solids) in water, conductivity methods are frequently the first ones tried. Various applications recently described include boiler water and steam condensate purity (*225, 236, 242, 243*), and salt content of river water (*30, 451*). Air-borne sulfuric acid aerosols are determined conductometrically (*399*) by measurement of the sample continuously washed off the rotating anode of an electrostatic precipitator. A commercial laboratory ion-exchange column for mineral-free water (*280*) has a small conductivity indicator dial which reads directly in parts per million of sodium chloride of the eluted water. Grimes (*196*) has patented an electronic detector sensitive to small changes in conductance for the purpose of indicating the presence of water in gasoline in aircraft. Various gases, particularly sulfur dioxide, carbon dioxide, and hydrogen sulfide, are determined by bubbling the sample through water (*285, 433, 434*).

Potentiometry. By far the most used type of potentiometric measurement is that for the purpose of determining and/or controlling pH. A large amount of literature has become available recently in this field (*40, 44, 46, 70, 169, 185, 267, 274, 283, 284, 290, 339, 343, 360, 435, 473, 479*), and the general procedure of glass-electrode pH measurement has settled down to a more or less routine basis. A novel application (*163*) measures the pH of gastric juices in situ by introducing the glass electrode directly into the stomach of a dog. The adequate mixing of the gastric juices is accomplished by the use of an automatic aspirating and injecting device. The raw sewage chlorination is controlled automatically by readings from a recording potentiometer (*233*).

Two uses of automatic potentiometry for determinations other than pH have been described, one being a device for indicating changes in the composition of gases (*246*). The changes in composition are measured by the potential difference between two series-connected ionization chambers, one hermetically sealed and the other placed in the sample gas stream. Bickford (*29*) has described an electronic measurement of anesthetic in the human brain during an operation, based on the fact that the brain potentials increase as anesthesia decreases. When an emergency arises, such as shock or respiration failure, a warning signal is given and administration of the anesthetic is automatically stopped.

Measurement of Electric Current. When the magnitude of an electric current is used to measure the desired constituent, the analytical process may be called currentimetry. A recorder for measuring residual chlorine in water is now available commercially (*458, 459*). Several papers (*24, 417, 477*) have described the use of a dropping-mercury electrode for continuously measuring dissolved oxygen in flowing water or in sample gases bubbled into water. Connections are made which permit an extremely slow flow of potassium chloride solution through the bridge into the electrolysis cell.

A direct-reading polarograph for tetraethyllead in gasoline using antimony as the pilot ion has been described (*353*). Elofson *et al.* (*145*) have applied the dropping-mercury electrode to diazo chemistry. With it coupling rates, diazotization rates, and concentration changes can be continuously measured.

Measurement of Dielectric Constant. The high dielectric constant of water makes its determination in a wide variety of materials highly susceptible to capacitance measurements. A great deal of activity in this field has been reported and the principle seems destined for wide use in moisture determination of all types of essentially nonconducting solids or liquids. One manufacturer has recently made available a Capacity Dynalog for recording any variables which can be made to produce an electrical capacitance change (*338*). Radio-frequency voltages are impressed across two tuned circuits, one the measuring circuit and the other the balancing circuit. When the capacitances of the two are unequal, a signal results which is amplified and eventually drives a servomotor to adjust the balancing capacitance until the signal received by the amplifier is zero. In this condition the capacitances of the balancing circuit and measuring circuit are equal, and we have a measure of the dielectric constant of whatever sample is in the measuring circuit.

Comparative and critical studies (*230, 245*) emphasize the importance of correct calibration techniques and the effects of temperature and voltage fluctuations. Applications which have been described recently include the determination of moisture in paper (*155, 170, 388*), leather (*275*), butter (*123*), textiles and wood (*482*), sand, flour, and coal powder (*256*), and grain, flour, gunpowder, and clay (*73*). A number of portable moisture indicators of the push-button or pistol-grip style are also available (*67, 143, 323*).

The recording microwave refractometer developed by Birnbaum (see Refractometry section) measures changes in dielectric constants of lossless gases, liquids, and solids.

Measurement of Radioactivity. Industrial uses of various types of radioactive properties, though still outnumbered by applications in the life science fields, are increasing. A number of scientific instrument houses supply a wide line of automatic timers, counters, scalers, and computers (*27, 231, 232, 350, 438*) for various uses. One, for example (*27*), has an automatic scaling unit providing for a predetermined number of counts, and features an automatic timer to permit operation for a preset time interval (or a preset number of counts). It has a direct-reading scale which indicates the count directly as an illuminated number, thus eliminating interpolation and dial-reading errors. Brownell (*58*) has mentioned a new crystal detector instrument called a "scintillometer" for measuring gamma-rays, and thus uranium. It also distinguishes between uranium and thorium radiation.

Rymer (*395*) has described general radioactive tracer techniques in research and industry and emphasized the conditions necessary for successful identification, measurement of vapor pressure and complex mixtures, study of lubrication problems, and the value of selective activation of specimens in geology and prospecting. Another application includes a radioactive ore analyzer (*438*).

Methods involving irradiation of the sample with radioactive emanations are also finding increased usage. Beta-ray gages can measure weight per unit area (density) or thickness on production lines (*53, 438*). Advantages of beta-rays over x-ray or gamma-rays for these purposes include: function of weight per unit area and not atomic number; greater ionizing powers, permitting use of a much weaker flux of radiation; simpler source (no high voltages and complex circuits); and feasibility for extremely thin sheets. Friedman **et al.** (*174*) have patented a beta-ray device for determination of water in fuels such as gasoline.

Lipson (*297*) has a patent which describes a fast neutron bombardment of the sample to determine directly the amount of hydrogen present. The apparatus has wide applications in soil analysis and in geophysical exploration (petroleum).

DATA

More and more, analytical chemists and others dealing with analytical data, particularly from automatic measurements, find themselves with more information than they can use conveniently. The problem of how best to record the information and what to do with it, once it is obtained, approaches the proportions of a plague in many situations. The reviewers in the following discussion do not pretend to present a complete picture of how the problem of getting the utmost information out of analytical measurements is or may be solved. However, it seems desirable at least to consider ways in which data-handling automatons have frequently proved an invaluable aid.

Invariably, the data collected are for some specific purpose: In research it may be to prove what is going on in some chemical process or to indicate merely how much of what is present in a given system; in industry it may be to guide the manufacturer in his evaluation of his product during various stages of the process. In the latter case, the numerical data may be actually ignored or by-passed by the use of automatic control in which (usually) an electric current, proportional to the amount of desired constituent present, is caused to operate valves or other reagent-addition mechanisms to hold certain variables constant. The question of transferring the magnitude from the measuring element to the controller is a problem in itself (*35, 337*). Until the recent past, these variables have mostly been temperature, pressure, and time. However, chemical concentrations (notably pH) are increasingly becoming also directly controlled by the measuring element itself. Wiener in his book "Cybernetics" (*471*) makes the statement that "soon there will be wholly automatic factories with artificial brains keeping track of every process. They will order raw materials, store them, and route them through the plant. They will pay the bills, blow the factory whistle, and pay the help (if any)." While this statement sounds premature at this stage of industrial progress [particularly in view of Hammond's and Yardley's statements (*203, 478*)], the fact of semiautomatic chemical process plants is already with us, and the trend is certainly taking us further in this direction.

A large amount of excellent industrial literature is available describing various types of general photoelectric and potentiometric recorders (*43, 49, 86, 93, 96, 105, 149, 324, 342, 423, 429, 468*) for strip or circular charts. Authorities differ on the best type to use, but there are so many to choose from that one can generally be found for almost any particular use. One manufacturer (*286*) advertises simply an *X-Y* recorder where the variables to be recorded are converted to direct current signals and connected to the instrument, one to the horizontal axis and the other to the vertical. Sharp and Schreyer (*404*) have discussed the factors involved in obtaining clear, legible chart records (type of pen, ink, and paper, dotted or continuous traces, and maintenance requirements). A series of articles on "Recording Galvanometers and How to Use Them" (*100*) has been published. The use of cathode-ray oscillographs for particular purposes as recording light absorption spectra and polarographs (*412*) has been considered. One company (*99*) even has made available a "telereader" for speeding the reading of oscillographic traces. It is a combination of a "telecorder" and an I.B.M. punch unit, which records each reading together with identifying information, calibration factors, and correction constants on a punched card. The operator merely moves an adjustable cross wire to coincide with the desired point of measurement on the oscilloscope and presses a button, and the card is punched at a maximum rate of 50 per minute. (The manufacturer makes no recommendations of what to do with a possible total of 2000 cards obtained per work-week.) The use of punched card machines for rapid routine calculation of multicomponent mixtures from infrared data has been reviewed by Opler (*356*). The 3 minutes required for calculation of a ten-component mixture represent a substantial saving over the 15 or 11 minutes required by a desk calculator or analog computer, respectively.

The computing of numerical data, once obtained, may be handled by numerous types of computing machines. Wiener (*471*) discusses computers in their resemblance to the human brain. Any burden of calculation which can be removed from the brain can, of course, leave it free for other thought processes—e.g., imagination—of which machines at present are incapable. Memory processes seem to be currently the main problem in "thinking machines" (*437*), but the forecasting of the chemical and physical properties of a new compound before it is synthesized appears possible (given sufficient information).

Presently available computers include simultaneous equation calculators (*61, 101, 367*), curve subtractors, adders, multipliers, dividers, or integrators (*166, 296, 313*), and tristimulus integrators for color computing (*7, 110*). One new device (*8*) causes electronic computers to correct their own errors. An Italian computer (*121*) designed for solving problems in reinforced concrete structural design, but adaptable to other problems, solves five equations (each interdependent) in 5 seconds with one setting to give not one solution, but an infinite number from which the operator selects the most desirable. The device may be thought of as an assembly of many logarithmic slide rules, one for each of the algebraic expressions to be solved, which are geared together so that setting one variable automatically sets the other dials. Presumably the original setting could itself be accomplished automatically.

In summarizing, the reviewers would state that significant activity is evident in all fields toward the end of replacing both the human hand and brain by analytical automatons.

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Determination of Superoxide Oxygen

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A problem in progress in the authors' laboratory required a good analytical method for differentiating between superoxide and peroxide oxygen in solid materials. It was found that superoxide oxygen in such materials can be determined with reasonable accuracy by treatment of the solid with a mixture of glacial acetic acid and diethyl phthalate. No secondary decomposition of peroxide occurs. The method discovered should be of considerable value to workers in the superoxide field. It has already proved valuable in this laboratory in the solution of a problem involving synthesis of mixed superoxides-peroxides.

THE development in recent years of potassium superoxide, KO_2, as a chemical for air purification—i.e., the absorption of carbon dioxide and water vapor from the atmosphere with the concomitant liberation of oxygen—has greatly stimulated interest in the theoretical and practical aspects of superoxide chemistry. However, exact experimental work in many phases of research on superoxides has been hampered by the lack of a suitable method for the determination of superoxide oxygen.

Holt and Sims (*2*) first reported that potassium superoxide reacts with water vapor in accordance with the equation

$$2KO_2 + aq. = K_2O_2.aq. + O_2$$

The same reaction presumably takes place with liquid water at 0° C. (*4*). In theory, this reaction offers a rapid method for determining superoxide oxygen; in practice, however, it is impossible to avoid secondary decomposition of the peroxide formed and results are erratic and consistently high. (Decomposition of the peroxide has been attributed to local heating and the catalytic effect of hydroxide ion formed in the reaction.)

It has been demonstrated recently (*6*) that sodium superoxide (a paramagnetic substance), when in admixture with sodium peroxide, may be determined with reasonable accuracy by a magnetic method. The magnetic method, however, is considerably limited in scope. It is of little value if more than one diamagnetic impurity is present, or if the sample contains other paramagnetic substances.

Preliminary experiments (*5*) in the authors' laboratory on the decomposition of sodium peroxide–sodium superoxide mixtures by means of solutions of glacial acetic acid in carbon tetrachloride indicated that the oxygen evolved in such decomposition provided a semiquantitative measure of superoxide content. It was difficult, however, to determine the exact point at which release of superoxide oxygen was complete. The present paper describes the use of a glacial acetic acid–diethyl phthalate solution for the determination of superoxide oxygen. The results of experiments indicate that this solution quantitatively converts superoxides to oxygen and hydrogen peroxide. There is little, if any, release of oxygen by the secondary decomposition of the hydrogen peroxide formed. Thus, the procedure utilized would appear to be applicable to any mixture containing superoxide ion.