Instrumental Analytical Methods for Edible Oil Processing: Present and Future

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ABSTRACT

Current trends in analytical techniques for edible oil processing are reviewed. Major emphasis is placed on advances in instrumental and automated analyses. Future goals and priorities are also discussed. Some of the major analytical topics covered are: pulsed nuclear magnetic resonance, automated solid fat index, atomic absorption, automated active oxygen method, color, hydrogenation control, and gas liquid chromatography.

INTRODUCTION

Processors of edible oil have two levels of analytical requirements. First is the routine analysis of all products and basestocks. These are made to monitor plant operation and to ensure proper blending and final customer specification approval. These analyses include color, solid fat index (SFI), gas liquid chromatography (GLC), peroxide value (PV), free fatty acids (FFA), iodine value (IV), and biochemical oxygen demand (BOD). Oil purchasers then use these same analyses to determine if the incoming oil is within specifications for their particular application.

A second category of analyses would generally require greater sophistication for the purpose of technical back-up. These secondary analyses may be performed by a research laboratory, a centralized quality control laboratory, or, if the company is small, by an outside consulting laboratory. Analytical support equipment needed would have the capability of analyzing trace metals, soaps, polymers, mono- and diglycerides, emulsifiers, silicones, and *trans* isomers, as well as developing new analytical techniques. These analyses are used as investigatory tools to determine why products are failing, to evaluate competitive products, to observe product uniformity, to meet certain governmental or customer requirements, and to assist new product development or process changes. As processors increase their sophistication or as regulations or labeling requirements are broadened, these categories of analyses are expanded.

A third interrelated category regarding analytical laboratories these days is automation and laboratory data management using computers and intelligent analytical equipment. The demand required of today's laboratories has strained companies to the limit. Just 10 years ago, few laboratories had a GLC and fewer still worried about BOD load to the environment. In order not to employ an army of laboratory personnel to respond to these demands, analytical laboratories have had to adopt automation and computer assistance.

I will highlight recent innovative instruments and techniques in each of these three categories of analytical chemistry in the edible oil processing industry. This rapidly changing field will undergo accelerated change in the future. I will outline some priorities for change and make a few predictions.

NEW TECHNIQUES AND INSTRUMENTATION FOR QUALITY CONTROL LABORATORY LEVEL ANALYSES

Edible Oil Colorimeter

One of the most impressive new instruments was introduced officially at the 73rd AOCS Annual Meeting, Toronto, 1982. A number of laboratories have already adopted it. This instrument is the edible oil colorimeter (EOC) made by McClosky Scientific Industries, Inc. It is designed to conform to AOCS Procedure CC 13b-45, as well as European procedures. It is available in two versions: laboratory and on-line. The lab instrument allows the laboratory to determine automatically, depending on instrument settings, all aspects of oil color (see Table I).

TABLE I

Edible Oil Colorimeter Options and Ranges

Color or constituent	Range	Incremental units
Red "A" (AOCS red)	0-22 units	0.1 units
Red "L" (European red)	0-20 units	0.1 units
Yellow	0-40 units	0.1 units
β-Carotene (ppm)	0-20.4 ppm	0.1 ppm
Blue "A" or	0-1.7 units	
chlorophyll a (ppm)	0-1023 ppb	
Blue "B" or	0-1.4 units	
chlorophyll b (ppm)	0-512 ppb	

These ranges may be broadened by the use of shorter path length cells. While the instrument is capable of giving all of these data, some of the results are either/or situations, and in other cases, the instrument must be recalibrated, an easy step. Thus, the EOC will give red "A" and yellow, or with recalibration red "L" and/or β-carotene. As an option, the EOC will also give chlorophyll or blue values. However, the instrument has compatability for only two circuits. Thus, the laboratory must choose from the following combinations: chlorophyll a/b, blue A/B; chlorophyll a/blue A, etc., when instrument is purchased. If, for example, the chlorophyll a/b program is chosen, one would get chlorophyll automatically with the red and yellow, then with a quick recalibration could get the chlorophyll b.

The instrument has the capability of RS-232 interfacing, allowing the results to be forwarded to a laboratory database computer. This instrument, which has an adjustably heated sample chamber, represents a technological advance over two existing instruments: the Lovibond Tintometer, with which color measurements are made by a technician using color comparison to standard colored glasses, and the Lovibond Automatic Tintometer, which removed the color measurement from the responsibility of the laboratory technician and replaced it with the responsibility to read a moving pointer meter. Furthermore, as generally configured, these two previous instruments are only good for red and yellow measurements.

The current cost for the basic EOC is $4,615. We felt the instrument was well built and found it to give reproducible data which correlated well with the Lovibond Tintometer.

Rancimat

Brinkman Instruments has recently developed equipment to determine automatically the stability of oils. This instrument, the E 617 Rancimat, is based upon work done by Pardun (1), Zürcher (2) and others (3,4). They found that the conductivity of deionized water is increased by trapped volatile oxidation products produced when an oil is heated under a stream of air or oxidant gas. Thus, the increase in conductivity is related to the stability of the oil. This instrument can effectively replace the current AOCS Procedure Cd 12-57, which is dependent upon manual titrations for peroxide value taken at intervals carefully chosen so that the end point or induction period is not overshot.

To use the instrument, 2.0 g of oil are added to a heated (120 C) sample tube connected on one side to a source of air which is bubbled through the oil and connected on the other side through a cell containing 50 mL of deionized water (Fig. 1). The conductance of this water is measured automatically over time on a strip chart recorder. Independent cells permit the analysis of 6 oils at a time. A typical oxidation curve is shown in Figure 2.

Normally, one observes an induction period followed by a rapidly rising response as oxidation of the oil is accelerated. This induction period corresponds to the stability of the oil. The induction period may be correlated with data from the current AOM procedure or may be used directly to set up specifications.

Our laboratory acquired an E 617 Rancimat for evaluation. We investigated various parameters: oxidant flow, heat, oxidant type, oil type, and oil containing pro- and antioxidants. Summarizing these studies, we found the analytical method to give very reproducible results over time with no erratic behavior. Samples of the same hydrogenation class gave uniform results from sample to sample.

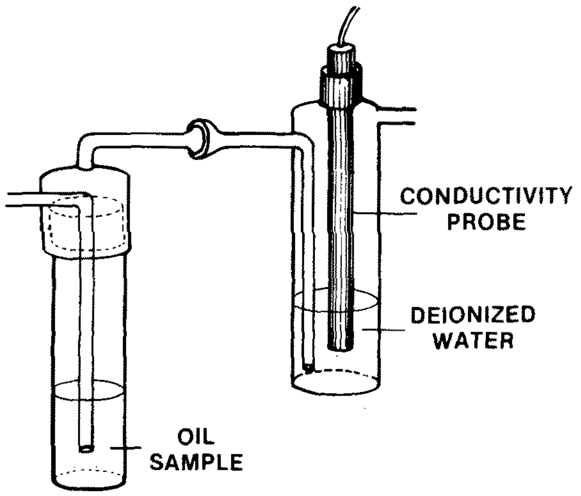

FIG. 1. Rancimat cell flow diagram.

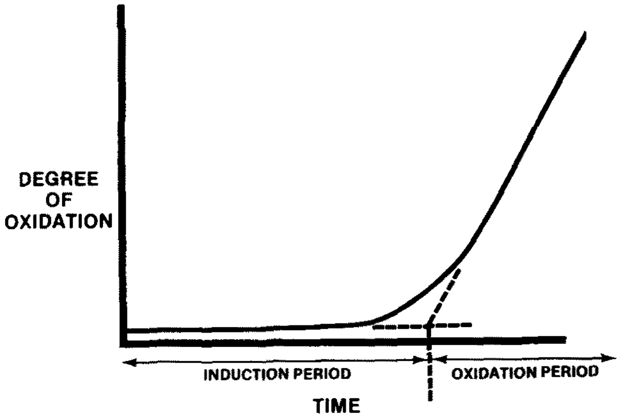

FIG. 2. Typical oxidation curve.

The method was able to distinguish, in a marked and predictable manner, those oils to which pro- and antioxidants had been added.

The instrument as it is presently configured does not have an RS-232 interface, which limits somewhat its capability regarding laboratory computerization. It is priced at $13,900, accessories included.

J.M. deMan (5) has described a homebuilt unit very similar to the Rancimat.

Mettler Dropping Point

This instrument has become a standard in most quality control laboratories. The AOCS has published it as a tentative method (Cc 18-80). Basically, a cold solidified sample is warmed by temperature programming until it becomes sufficiently fluid to flow. When the sample flows, it trips a photoelectric circuit which records the temperature. We have used this instrument since 1975 and found the analysis to correlate well with Wiley melting point (AOCS Method Cc 2-38). The current price for the Mettler FP 5 control unit and FP 53 dropping point furnace is $7,410. It has no RS-232 output.

Automated SFI

From its beginnings in the early1930s, dilatometry, commonly referred to as SFI, has become the preeminent analysis in the fats and oils laboratory. It is the single most important criterion for basing specifications on the rheological properties of fats, namely melting behavior and crystalline structure. However, despite its importance, it is the most labor intensive and costly, regarding maintenance and space, of all analyses run. No wonder it has been the target of highest priority for replacement with updated technology.

In the early 1970s, the AOCS established task groups to perform interlab collaborative sudies on various promising methods, namely differential scanning calorimetry (DSC) and nuclear magnetic resonance (NMR) *(6)*.

The DSC dropped out of contention very early. Our experience provides typical reasons for the DSC's failure as a quality control instrument. Our laboratory obtained a DSC in late 1970 for the purpose of evaluating the technique as a replacement for SFI. It seemed an obvious choice because it measured the change in heat absorption vs the temperature of the sample programmed from one temperature to another. Thus, one could record a melting profile of a sample as it transversed through various crystalline states from a solid to a liquid fat (Fig. 3). Our laboratory was dissatisfied with the DSC technique for several reasons. First, since the DSC was dependent on the amount of fat analyzed, it was difficult to relate the data from the DSC curve to the weight of the fat without integrating over arbitrary temperature ranges. Reanalysis of the same fat was not as reproducible as SFI. The worst handicap of this analysis was the sample limitation. The instrument required samples in the 10 mg range, weighed accurately on a microbalance. This would not be recommended for a quality control laboratory.

Finally, the DSC gave too much information to lend itself easily for quality control. Each blend, each degree of hydrogenation of base stock, each oil type (soy, corn, etc.) had its own distinctive curve. Thus, the DSC has only found use in research laboratories where very precise thermal histories are needed, for example, to mimic the melting behavior of cocoa butter.

Only the NMR method had the potential for achieving the long sought-after goal of replacing the SFI dilatometric method. Early NMR work began with the use of wide-line NMR which became commercially available in the 1960s. Pulsed NMR developed later and became available in the early 1970s.

The AOCS recognized the potential for NMR and established an ad hoc task force in 1970 (6). A symposium on NMR was also presented at the AOCS Meeting in Minneapolis, 1970 (7).

Collaborative studies encountered initial reproducibility problems, but with optimization, the standard deviation was reduced to 1-2%. In 1972, the committee was prepared to submit a method based upon the wide-line studies to the Instrumental Techniques Committee for inclusion in the "Official and Tentative Methods of the AOCS". By that time, pulsed NMR instruments had just been commercially introduced. Comparison studies indicated that the pulsed NMR technique was superior to the wide-line method (8).

The AOCS subcommittee was planning to proceed with the NMR program, but instead lapsed into inactivity until 1979 when the committee was reactivated. The impetus for this was the commercial development of a pulsed NMR specifically for solid fat measurement, the Praxis SFC-900 Spectrometer (9) (see Fig. 4). In the interim, a number of studies comparing and utilizing wide-line and pulsed NMR were published (10-15).

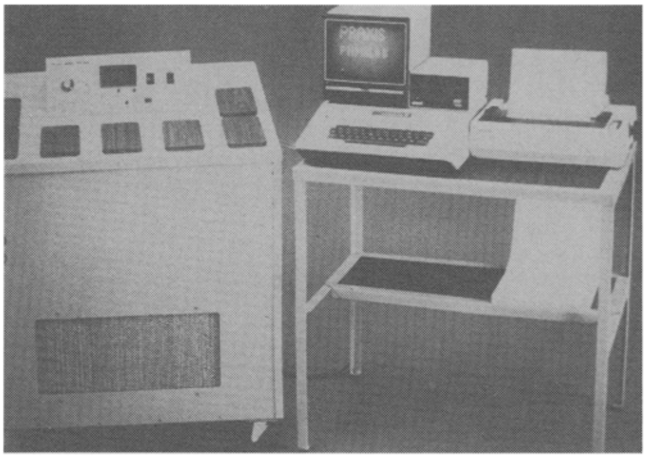

FIG. 4. Praxis SFC-900 Spectrometer for solid fat measurement.

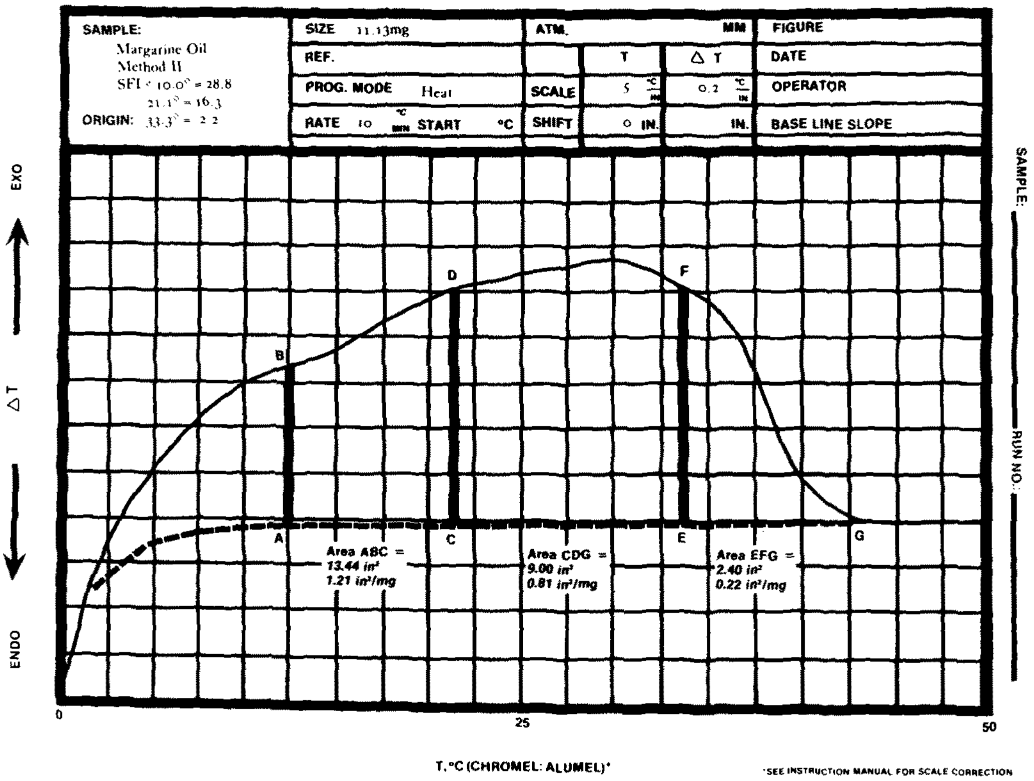

FIG. 3. Melting profile of a margarine oil.

The committee, headed by Jack Melema with major support from Brian Madison and Bob Manning, organized and developed procedural methods based upon standard fat mixtures consisting of blends of olive oil and tristearine. In 1981, the AOCS adopted the method as a recommended practice based upon pulsed NMR (Cd 16-81).

Mark Matlock, of our laboratory, has developed computer programs based upon an Apple II computer for prompting the analyst and automatically acquiring and calculating the data (16). This system is currently being marketed by the Praxis Corporation. Presently, there are about 20 pulsed NMRs in use in the USA. Very few are being used as quality control instruments. Most are still under development in research laboratories. Our laboratory has a Praxis SFC-900, which we are using for quality control in our packaging plant. Along with several others, we are evaluating the IBM PC 20 pulsed NMR (Fig. 5). In general, we have been most pleased with the results.

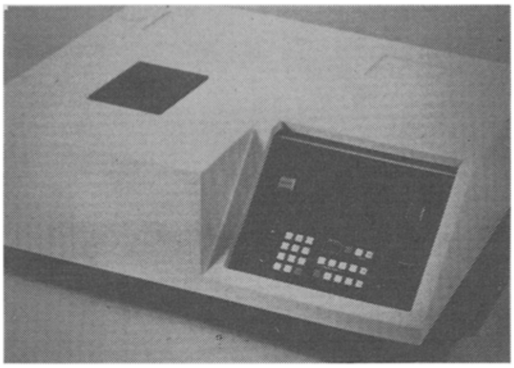

FIG. 5. IBM PC 20 pulsed NMR instrument.

When comparing the two commercial pulsed NMR instruments, each has advantages and liabilities which must be considered.

Praxis SFC-900

Advantages

- Set up specifically for SFC with 6 temperature ports containing 5 magnets and probes for liquid readings at each SFI temperature
- Self-contained single unit
- Capable of RS-232 interfacing
- Utilizes cheap, disposable glass sample tubes

Disadvantages

- Probes set at low temperatures are susceptible to moisture condensation and corrosion problems
- Five probes present 5 times the number of circuits, etc., which can go bad or need optimization
- The heating/cooling system is based upon coolant flowing from the coldest to the warmest port such that variation in one causes variation in all downstream
- Coolant flow has been erratic at times

IBM PC 20 Minispec

Advantages

- A single optimum magnet and probe
- Program routine may be added as an electronic chip
- Capable of RS-232 interfacing

Disadvantages

- Requires external heating/cooling baths or blocks
- The probe is extremely susceptible to temperature changes causing irreproducible results or rapid sampling

Both Praxis and IBM are continuing to upgrade their instruments. Presently, Praxis is planning on digitizing their signal directly, which will replace their analog output and related signal averagers. IBM is working on a variable temperature probe to allow heating/cooling quickly to any desired temperature for SFC analysis. The Praxis SFC-900 is $21,000 without computer accessories or $26,000 with accessories. The IBM PC 20 is $23,000 with external heating/cooling blocks and controllers extra. These two instruments would be similar regarding sample throughput per hour.

Lastly, before leaving the subject of SFI, one other instrument has appeared which has the ability to produce values correlatable with SFI. This is the Anton Paar density meter described by Mills and von de Voort (17). It would not lend itself to a quality control laboratory environment for two reasons. First, the instrument is very delicate; and second, it has a tendency for fats greater than 35 SFI to give false readings due to contraction of the fat on cooling to form cracks, etc.

Automated Iodine Value (IV) Analyses

Recently, an infrared (IR) technique has been published for determination of total unsaturation of oils (18). Using the absorbance at 1658 cm^{-1}, various vegetable oils were analyzed for IV within 1% of known values. If one particular oil was used as a standard, e.g., soybean oil, that oil could then be analyzed directly. If another oil type was to be determined, e.g., corn or peanut oil, using the soy oil standard a correlation factor was needed. This technique utilized a liquid sample cell of 0.1 mm path length and required thorough cell cleaning between analyses.

Our laboratory collaborated with Foxboro, Inc., using their Miran-980 Infrared Analyzer equipped with a multiple internal reflectance (MIR) cell. Iodine values of various oils were determined. Figure 6 shows a plot of absorbance vs iodine value. With the MIR cell, a technician merely spreads the sample over it. It may then be cleaned off rapidly by wiping after analysis. Both the Miran-980 and the spectrophotometer used in the first study are in the $18,000 range and have an RS-232 interface.

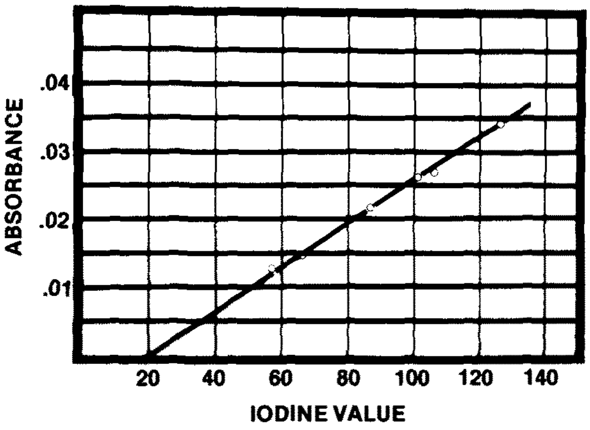

FIG. 6. Infrared analysis of iodine value.

NEW TECHNIQUES AND INSTRUMENTATION FOR TECHNICAL BACKUP LEVEL ANALYSES

Trace Metal Analyses

Improvements have been made in methods over the years. Initially, wet chemical analyses were used and improved. In the late 1960s, flame atomic absorption spectroscopy was introduced. The AOCS issued it as a tentative method in 1975 (Ca 15-75). In the early 1970s, the graphite furnace was found to be a vast improvement over the flame. The AOCS gave this method tentative status in 1979 (Ca 18-79). Optimization of the graphite furnace technique has been accomplished with the use of an autosampler. Recently an increasing array of new techniques have become commercially available, such as plasma emission spectroscopy (ICP and DCP). These instruments offer the advantage of multielement sequential or simultaneous analysis. All of the above techniques offer advantages and disadvantages which must be taken into consideration prior to purchase. The laboratory must choose a technique which best fits its particular needs. Frequency of analyses, number of samples analyzed, cost of the instruments, and costs of operation and technical personnel to operate them must be reviewed and anticipated. Table II can serve as a guide.

Thus, infrequent analyses might justify only wet chemical procedures, while frequent multielemental screening at reduced sensitivity might necessitate an ICP capable of simultaneous analyses. One should always be aware of hidden costs for some of these techniques. For example, ICP and DCP spectrometers can consume up to $4,000 per year in argon alone (20).

Our laboratory has balanced sample demand and sensitivity vs low manpower requirements. Therefore, we utilize a graphite furnace AA which has been modified in data handling capabilities such that all results are automatically logged, calculated and reported in memo form.

Geometrical/Positional Fatty Acid Isomer Compositional Analysis

Due to increasing conern among researchers about the effects of *trans* isomers on the diets of humans, more information on the compositional analysis of commercial fat is being requested (21). Regulation in some countries require package labeling to include *trans*-isomer content. Several techniques have been developed and improvements on techniques made. Of these, gas liquid chromatography is the most specific in that it can give information on specific isomers.

Several GLC procedures are available: packed column—for low resolution; or capillary/WCOT column—for high resolution (22-24). The two other instrumental methods applied to this analysis are limited somewhat in that they give only % total *trans*. The first is the infrared spectrophotometric method. The AOCS has written this up as a tentative method (Cd 14-61). Madison et al. (25) have recently published an improved technique, for which it would be helpful to have an IR spectrophotometer capable of storing and subtracting spectra.

The second technique is an old one, but it is still worthy of renewed evaluation. This is the Raman spectroscopic analysis of *cis/trans* isomer composition by Bailey et al. (26). Its only major drawback is expense. Instruments are in th $50-70,000 range.

LABORATORY AUTOMATION AND DATA MANAGEMENT

Laboratory Automation

From its early beginnings, the goal of laboratory automa-

TABLE II

Comparison of Instrumentation for Trace Metal Analysis

Analytical technique/instrument required	Cost	Advantages	Disadvantages	Comparative detection limits (ppm) (19)		
				Copper	Iron	Nickel
Wet chemical analysis UV/visible spectrophotometer	$7,000 or less	Inexpensive Versatile	Preconcentration needed Very labor intensive	0.005	0.01	0.05
Flame atomic absorption spectrophotometer	$32,000	Versatile	Preconcentration needed Labor intensive	2	5	8
Furnace equipped atomic absorption spectrophotometer	$40,000	No preconcentration needed	Very skilled operator needed	0.005	0.01	0.05
Furnace and autosampler Equipped atomic absorption spectrophotometer	$48,000	No preconcentration needed Automated analysis Low skill required	Expensive	0.005	0.01	0.05
Inductive or direct-coupled plasma emission spectrometer	$80-150,000 and up	Simultaneous or sequential multielement capability	Preconcentration needed Expensive Costly to operate	2	25	15[a]

[a] Dijkstra, A.J., and D. Meert, JAOCS 59:199 (1982) have reported improved detection limits.

tion has been to mechanize routine steps in the laboratory to improve accuracy and efficiency. One of the earliest automated systems was offered by Pope Scientific, and was a modified shotgun shell loader used to dispense a proper amount of catalyst for Kjeldahl analyses. Presently, laboratory automation has become an area of science of its own. World Trade Press began publishing the quarterly, "Journal of Automatic Chemistry," in 1978. GLCs, HPLCs, and, as mentioned earlier, AAs all now have autosamplers as an option, normally in the $10,000 range.

One of the largest growth areas in automated chemistry is robotics. Zymark Corporation has a robotic system specifically for chemical sampling/handling/analysis based upon a programmable arm/hand (see Fig. 7). The arm can attach two types of hands: a general purpose grasping hand, or a precision microliter syringe hand.

The arm/hand then dispenses, dilutes, dissolves, or transfers samples from station to station where they are filtered, extracted, centrifuged, weighed, derivatized, digested, or analyzed. The system is capable of complete analysis from sampling, through sample preparation, to analytical measurement and data reduction/documentation. The base cost for the system is $16,000. Total cost will all current options is $28,400. Robotic arms are available from other manufactuers. Microbot, Inc., has an arm with grasping hand for $13,000. Seiko Instruments robotic arms/hands range from $5-11,000. IBM markets one beginning at $26,000.

A robotic system would be ideal to adapt to the Praxis or IBM pulsed NMR for automated "solids" measurement. After a technician had placed the samples in tubes and logged them in, everything else would be automatic.

Laboratory automation is also making greater use of a technique referred to as flow injection analysis (FIA). Early autoanalyzers, of the Technicon type, were flow interrupted analyzers in which the stream was segmented and interrupted by a series of air bubbles. This segmenting was felt necessary to prevent sample contamination or memory effects, promote mixing, and prevent sample dilution. Flow injection analysis, based upon unsegmented flow, was introduced in the early 1970s and has become a widespread established technique. It allows for increased sampling rate —100-300 samples/hr, lower solvent/reagent usage and disposal, and easier sample manipulation with no degassing nor peristaltic pumps to maintain. FIA systems are best compared to HPLC where narrow bore tubing is used; precise volume injection of samples is maintained, and packed bed reactors or separators are analogous to HPLC columns.

One procedure using FIA for the automated determination of free fatty acids has been published by Lars-Gösta Ekström (27). A thiocyanate method for determining the peroxide values of lipids using segmented flow was published in 1969 (28). This would lend itself readily to FIA. Bittner et al. (29) have developed an automated system for esterification preparation for GLC analysis.

FIA systems may be assembled component-wise in much the same manner as one would put together pumps, columns, and detectors for HPLC analysis. Some complete systems are available off the shelf. One such system is the Lachat Quik Chem™ System IV. A basic system without microprocessor is $14,000. Microprocessor-equipped single chemical (one detector/analyte) system is $20,000. Multichemical systems are available.

Laboratory Data Management

There are several commercially available computer systems specifically designed for the laboratory. Hewlett Packard has marketed the 3350 series Laboratory Automation Systems for a number of years. It is designed to interface a number of instruments via a digital transmission loop. This loop design allows remote analog to digital converters to be connected to the system by running a single line to the first instrument. The line is then run from the first to the second, and so on. Finally, the loop is brought back to the computer from the last instrument wired in. This design minimizes cable runs, but the loop cannot be broken without disrupting the entire system. The HP 3350 series uses the HP-1B interface, also known as IEEE-488. Many instruments use the IEEE-488, but it is far from universal. The interface that comes closest to being universal is the RS-232. Almost all computer terminals use this interface; thus, it is almost always present in a computer or lab data system.

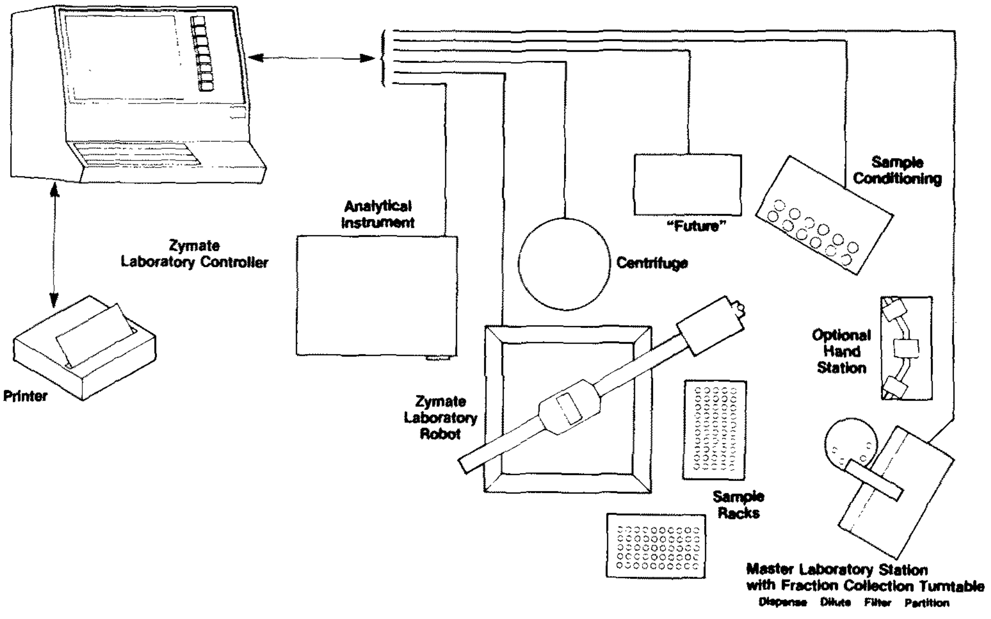

FIG. 7. Zymate™ Laboratory Automation System.

Perkin-Elmer markets the LIMS 2000 Laboratory Information Management System, which uses RS-232 to communicate to instruments. The philosophy behind Perkin-Elmer's system is their use of data stations. Using local intelligence, an integrator with communications ability, one can still be operational despite a failure in the central system. For example, in this system, if the central processing unit (CPU) is down, one could still use spectrophotometers (AA, UV-visible, IR). However, in this situation, chromatographic peak detection and integration is not possible without local intelligence. This function is provided by the data station.

This is an example of distributed intelligence, which is an important consideration when buying a lab data management system. Another important consideration is the RS-232 interface, which has been chosen as the communications link by most instrument manufacturers.

The main advantage of the Perkin-Elmer or Hewlett Packard system is that the software has already been written by the manufacturer. This software generates reports and performs sample data base management, as well as data logging functions. IBM has recently introduced a laboratory specific system. Others can be anticipated in the future. The present cost of these systems is $80-100,000 and up.

Another alternative is to purchase a general purpose computer and write or purchase the software. Many large companies have chosen this option in the past, because, until recently, the selection of laboratory data systems was limited. At our laboratory we chose this option because of the great flexibility it offers. We have designed our system around a Digital Equipment Corporation (DEC) PDP-11/24. We were able to take advantage of a number of programming languages, such as Fortran 77, Basic, APL, and Macro-assembler to aid in the development of the software. Also, we have a good data base management language, Datatrieve-11, where our users can easily create their own special purpose data bases. Our system, as it was initially configured, cost in the $40,000 range.

In a laboratory with a number of autosamplers functioning, sample throughput can be hundreds per day. Managing this volume of information is a considerable task. With a laboratory data system generating reports, memos and plots of data, the cost can easily be justified.

FUTURE TRENDS

It is obvious that routine analyses are becoming more mechanized and the human element minimized. As edible oils are refined and hydrogenated, three important process control points stand out as most critical: color, FFA, and degree of hydrogenation. Increasingly, these three analyses will move from the laboratory to on stream direct monitoring. Indeed, with the EOC mentioned previously, on-line analysis is presently available.

However, the most variable and most important step, hydrogenation, is where most effort will be placed on developing on-line instrumentation. Continuous infrared analysis during hydrogenation would give much of the needed information critical for optimized product quality by enabling operators to follow the degree of total unsaturation and percentage *trans*-isomerism on an instantaneous and continuous basis. Automatic feedback loops controlling hydrogen gassing, and other parameters would allow improved control to keep the hydrogenation directly on course.

Regardless, as analytical chemists work toward these goals, many challenging and interesting problems lie ahead.

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