

## COSMETIC KNOWLEDGE THROUGH INSTRUMENTAL TECHNIQUES\*

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TRADITIONALLY, the cosmetic field has been a very difficult one for the chemist and analyst. A study of the development of the cosmetic industry, however, shows the increasingly large part that science has played in it. The science referred to is made up of many parts, such as dermatology, physics, chemistry, toxicology, etc., but it is probably the science of measurement as much as anything that is lifting the cosmetic industry from the slough of empiricism and setting it firmly on its feet as a field of genuine scientific endeavor.

Lord Kelvin said, "If you can measure that of which you speak, and can express it by a number, you know something of your subject; but if you cannot measure it, your knowledge is meagre and unsatisfactory." Unfortunately, cosmetics have offered many examples where it has not been possible to "measure that of which you speak."

Historically, cosmetic research can be divided roughly into three phases. In the first, the emphasis was on the gross physical properties of importance to cosmetics, such as color, texture and particle size. During this period many vague subjective terms, such as "oiliness," "creaminess" and "smoothness" were in vogue, but apart from rough classifications of physical properties very little actual measurement was involved.

The second phase was stimulated by the rapid development of the chemical industry, with a resultant realization of the importance of product control methods and of specifications for the purity of raw materials and of finished products. The recent availability of synthetic materials and their use to replace natural products were also factors in this new awareness of the importance of chemistry to cosmetics. The chemical nature of fats and waxes was realized to be important to product performance and stability, acid numbers, iodine values and saponification numbers became valuable measurements when their correlation with such properties was established.

During this period the emergence of hair waving based on scientific

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principle occurred. The mechanical phase of hair waving was supplanted by the chemical phase (1). Manual dexterity with the hot curling tongs was replaced by mental dexterity in the cold light of scientific research. This led to the seemingly paradoxical use of mercaptans in cosmetics (2), a development which appeared to fly in the face of the entire experience of the cosmetic industry. These mercaptans have been used in waving lotions and depilatories in a powerful demonstration of the superiority of the scientific method over curling iron, razor blade, tweezers and depilating wax.

The third phase, which we have entered but comparatively recently, can be called the "era of physico-chemical measurement," a development which should make Lord Kelvin rest more easily. We have seen the gradual development of measurement techniques to aid cosmetic research in control work and in the evolution of new processes. We have pH, colorimetric and viscosity measurements on the one hand, and empirical measurements for detergency, foam stability and emulsion stability on the other. Probably the uses in analysis have had most emphasis, but the new instrumental techniques are also very valuable for determining the effects of cosmetics upon hair, skin and teeth. They show the functioning of processes, the absence of undesirable effects, the creation of desirable effects and the way to even better cosmetic products.

It is important these days to show that cosmetic products not only cover blemishes and change the color of the skin and hair, but also that they produce soft and smooth skin, better combing, increased luster and improved hair manageability. Unfortunately, methods for measuring these properties are not always at hand, and the problem of measurement arises. How should the measurement be made? By human senses or by machine? On fundamental properties or on some empirical basis?

Before attempting to answer these questions, certain generalities, often overlooked, about instruments should be considered:

(1) Instruments are developed for the convenience of man. They are designed to give him information more conveniently and more accurately than he could get the same results by hand.

(2) An instrument is a measuring device which can give information on three levels: (a) bulk properties, (b) molecular properties and (c) atomic properties. Most instruments can be classified accordingly.

(3) An instrument is designed to fill a gap in knowledge. The instrument for a given application is chosen according to the type of knowledge that is needed to solve a given problem.

(4) The area where the knowledge is needed governs the design of the instrument, rather than of the instrument governing the field of application.

(5) The results given by an instrument will be meaningful only in re-

gard to the conditions of the measurement employed. When different instrumental approaches are used to measure a certain property or effect of a substance, all the results obtained may be equally valid; but only some of these results will be useful.

Useful results are often the hardest or most expensive to obtain. This is particularly true in cosmetics where so many subjective terms are current. Ultimately, a subjective term has to be measured subjectively, but the instrument can play a valuable part if some correlation can be established between physical measurement and subjective response to a cosmetic product. Cosmetic research at Evans Research and Development Corporation has been greatly aided by a variety of techniques, some common and some less well known.

### PAPER CHROMATOGRAPHY

Paper chromatography within a space of ten years has grown from nothing to one of the most important methods of analysis in the whole

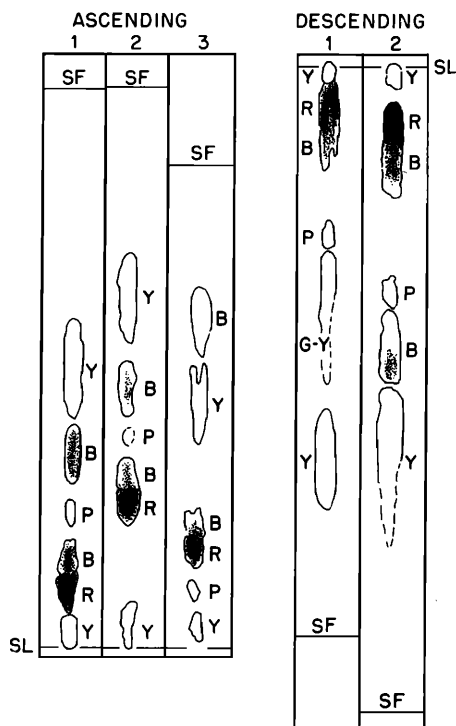


Figure 1.—Paper chromatogram of brown hair dye. SL = starting line, SF = solvent front, R = red, B = blue, P = pink, G-Y = green-yellow, Y = yellow, 1 = 4:1:5 *n*-butanol-acetic acid-water, 2 = 100:20:44:1 *n*-butanol-ethanol-water-ammonium hydroxide and 3 = 4:1 phenol-water.

field of chemistry. For example, it can be used to demonstrate how a variety of common writing inks consist of a number of colors. The inks are spotted onto ordinary filter paper and allowed to dry. The paper is suspended from a trough containing an organic solvent which flows by capillary action down the paper. The dyes in the writing inks have different solubilities in the solvent flowing past them and different affinities for the filter paper. As a result, they migrate from the starting point at different rates so that after a few hours the mixture is resolved into its components. These can usually be identified chemically or spectrophotometrically or by the rate they have moved down the filter paper. The entire apparatus is kept in a sealed glass cylinder to prevent evaporation of the solvent from the paper.

From dyes in writing inks it is a short step to dyes in hair coloring compositions. Chromatograms of a commercial brown hair dye are shown in Fig. 1. To ensure complete resolution, a number of solvents were used to examine the dye mixture. These different solvents caused the dyes to migrate at different rates. This is very useful for identifying unknown constituents, as it is a very characteristic property.

Dyes are fairly easy to separate because they are often quite similar in chemical composition. Oddly enough, it is the mixtures containing unrelated substances that often give the most trouble in paper chromatography. A good example of such a mixture is a waving lotion which might contain a

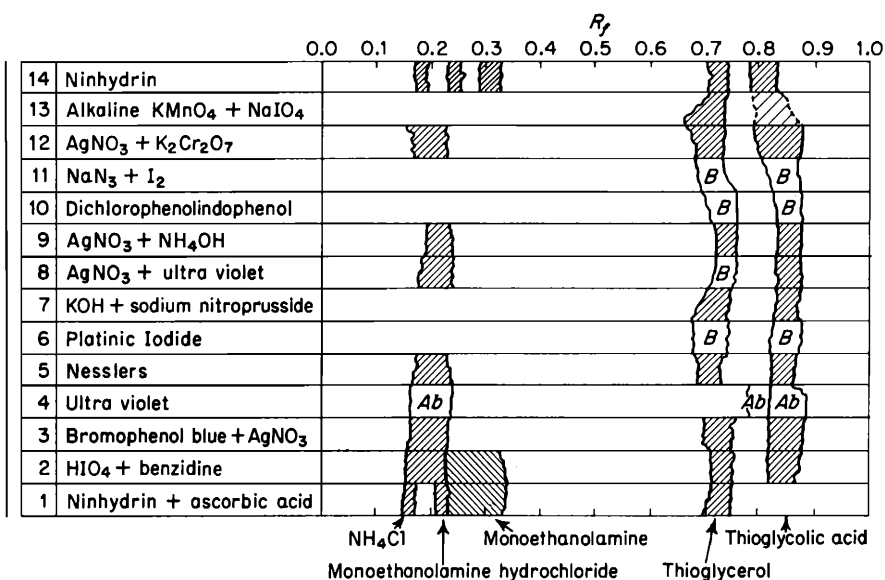


Figure 2.—Copy of a typical paper chromatogram of a waving lotion.  $R_f$  = rate of flow value, Ab = absorption and B = bleach.

mixture of mercaptans and bases. Figure 2 shows a diagram of a paper chromatogram of such a mixture. Since the components have no color of their own, they have to be visualized by using chromogenic reagents. These are usually sprayed onto the paper to locate the separated constituents of the lotion. A large variety of visualizing agents (up to 19) are used to make sure that all the substances in the mixture are detected. The paper is cut into strips, visualized and then reassembled to give the picture shown in Fig. 2. The positive and negative reactions of each substance are very useful in identifying the components. Space does not permit giving all the experimental details here, but it is hoped to publish this work separately.

### GAS CHROMATOGRAPHY

The principle of gas chromatography is identical with that of paper chromatography. A mixture of substances is made to move as vapors through a column containing an inert powder, such as crushed fire-brick, which is coated with a high boiling liquid. The vapors are carried through the column by a carrier gas, usually helium. They move at different rates depending on the temperature of the column and the solubility of each vapor in the high boiling liquid coating and take different times to pass through the column. A sensing device continuously compares helium, the gas entering the column, with the gas leaving the column. If any substance besides helium comes off the column, the difference is noticed, and an electrical signal is sent to a strip-chart recorder. The resulting peaks each represent at least one compound. When analyzing complex mixtures, one peak may often represent more than one compound. Thus, rechromatographing material, especially that represented by an early eluted peak, on a column bearing a different type of high boiling liquid often will reveal it to contain many substances.

Gas chromatography has a very important variable not possessed by other forms of chromatography, namely temperature, and, by using high temperature apparatus, oils boiling even in the 250–300°C. range can be separated.

Gas chromatography has been used for the separation of perfume constituents and flavoring substances. The tremendous power of this method was illustrated by the work of Dimick and Corse (3) on strawberry flavor, which they were able to resolve into over 30 components even though they found it only occurred to the extent of about eight p.p.m. in the strawberry.

As in any new method, precautions must always be taken. Figure 3 shows the results of using gas chromatography to examine an oil. The oil was in toluene solution so it seemed logical to assume that the big peak was toluene and that the smaller ones were constituents of the oil. However,

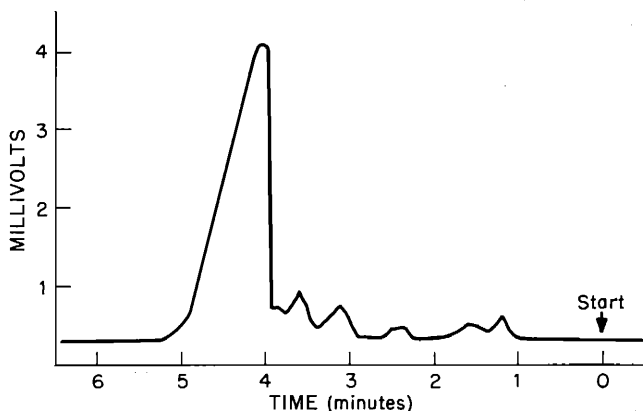


Figure 3.—Gas chromatogram of an oil in toluene solution. Carrier gas, helium; flow rate, 65 ml./min.; temperature, 153°C.; stationary phase, celite coated with silicone oil; column length, 2 meters; sample volume, 0.02 ml.

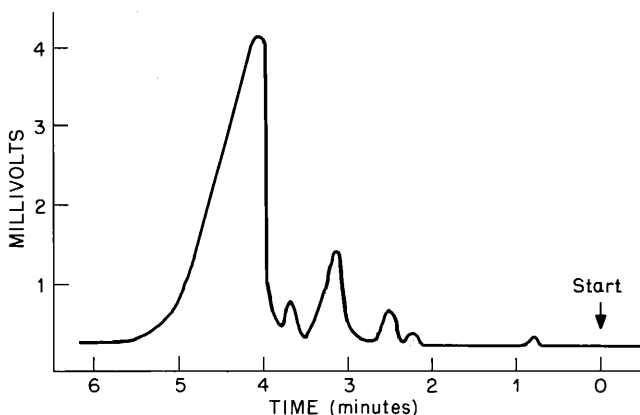


Figure 4.—Gas chromatogram of "pure" toluene. Carrier gas, helium; flow rate, 65 ml./min.; temperature, 153°C.; stationary phase, celite coated with silicone oil; column length, 2 meters; sample volume 0.02 ml.

when "pure" toluene was examined by gas chromatography, it was discovered, as can be seen in Fig. 4, that many of the small peaks resulted from the so-called "pure" toluene. This is probably true for many of the things which in the cosmetic industry today are called "pure." Many off-odor problems, lack of uniformity, and even allergenic reactions might be traced back to the starting materials. It is well known that "pure" compound A from supplier B often cannot be used in a formulation to replace "pure" compound A from supplier C. Here is a source of vexation that might speedily be removed if chromatographic specifications could be set for certain materials.

Whenever a new method or technique is announced, there is, regrettably, a slavish inclination to follow in the footsteps of the pioneers and possibly to push on a few more paces into the unknown. It is important, however, to step back and examine this new development to see if, in some other way, it could better be turned to one's specific needs and problems. The advent of gas chromatography affords a good example.

It has been reported (4) that good separations in gas chromatography can be achieved if the combination of inert support and high boiling liquid is replaced by the detergent "Tide" (The Procter and Gamble Company), and it has been found, indeed, that useful separations can be performed with it in the column. Other common household detergents have been examined, and it has been found that they, too, can be used. The separations given by these detergents are not of the same degree. If a standard mixture of alcohols and esters is separated by each of the detergent columns, different patterns are obtained on the recorder chart. Thus, detergents might be identified in a novel way by packing the unknown detergent into a column and using it to separate the standard mixture. The pattern obtained under standard conditions might then be matched with one given by a known detergent. Similarly, surface active agents, such as the polyoxyethylene ethers and esters, when used as the inert liquid support in a chromato-

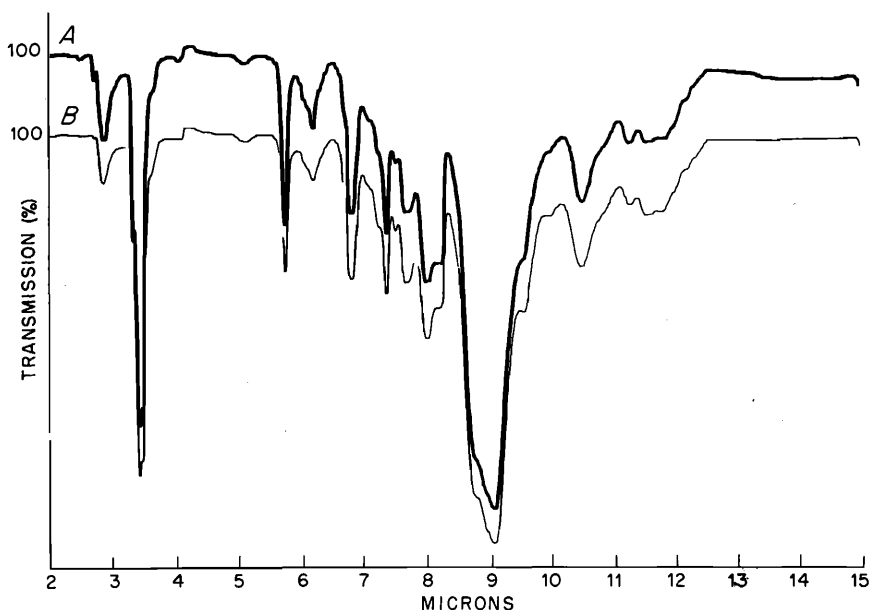


Figure 5.—Spectra of G-2162 and Tween 80. *A* = Tween 80 and *B* = G-2162. Both solutions were 5% by weight in chloroform. The spectra were obtained on a double-beam spectrophotometer.

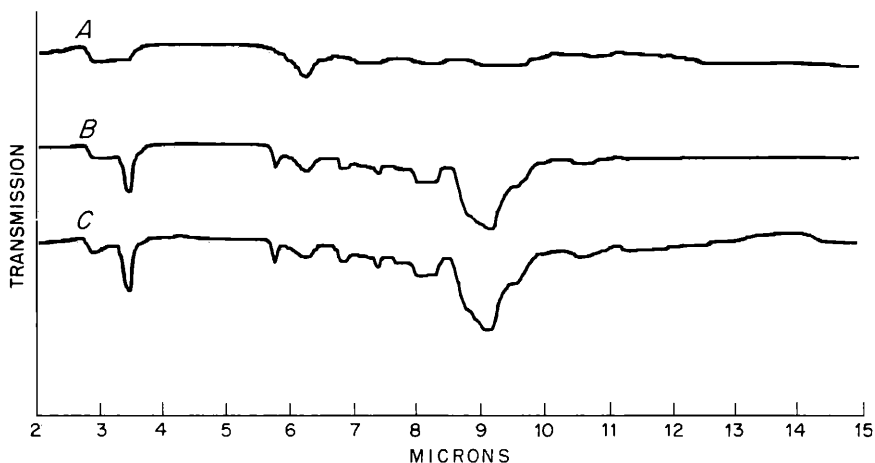


Figure 6.—Spectra of G-2162 and Tween 80 run differentially. *A* = base line Tween 80 *versus* Tween 80, *B* = 0.25% G-2162 in Tween 80 *versus* Tween 80, *C* = 0.5% G-2162 in Tween 80 *versus* Tween 80. All solutions were 5% by weight in chloroform. The spectra were obtained on a double-beam spectrophotometer.

graphic column, can be characterized by their resolving powers for a standard mixture. Needless to say, there are much more direct ways of analyzing detergents and surfactants, but it serves as a useful illustration of how man should direct the machine, and not the reverse.

#### INFRARED SPECTROMETER

If you looked through the last ten years of *THE JOURNAL OF THE SOCIETY OF COSMETIC CHEMISTS* and of the *PROCEEDINGS OF THE SCIENTIFIC SECTION OF THE TOILET GOODS ASSOCIATION*, you would find that papers on the use of the infrared spectrometer outnumbered those on any other instrumental technique, even though the first reported use of this instrument in these journals does not appear until December, 1952 (5). It would seem, therefore, that the cosmetic industry was about ten years behind the chemical industry in its acceptance of and use of this machine (6). The inability of the machine to measure directly those properties of a cosmetic product, which can be tied to consumer acceptance of the product, may have been a factor in this delay. However, the enormous benefits to be derived in control work, both of raw material and of finished product and in analysis of competitive products are surely appreciated today.

Figure 5 shows the infrared spectra of G-2162 (Atlas Powder Company's polyoxyethylene propylene glycol monostearate) and Tween 80 (Atlas Powder Company's polyoxyethylene sorbitan monooleate). There are some differences, in spite of the over-all similarity of the spectra, which might be used to look for a small percentage of one in the other. For the



best chance of detecting minor traces of one in the other, the unknown is run differentially against the pure known. (A double-beam machine is needed for this.) If they are identical, the absorptions in both beams cancel out and a straight line is obtained. If not, the difference is readily seen. Figure 6 shows the differences which can be obtained when run differentially.

#### CONSTANT RATE OF ELONGATION TESTER

A machine which has been of tremendous use in the research program on hair and other fibers is the Constant Rate of Elongation Tester—called the C. E. Tester for short. The instrument was made by G. F. Bush Associates (Princeton, N. J.) to meet the requirements of Evans Research and Development Corporation. An important feature is the arrangement for complete immersion of the sample under test. The fibers can be stretched anywhere between 50 per cent per minute and 1.25 per cent per minute, by varying the sample size and elevator speed. The strain gauge can be one giving 0.5 gm. full scale or bigger ones, up to 2.5 kg. full scale, can be used. Usually tensile forces are measured, but the machine is easily adapted to a variety of techniques, such as cycling, cutting or compression.

One of the most useful of the results given by this machine is the 20 per cent Index. A 12-hair strand is stretched 20 per cent in water. It is then

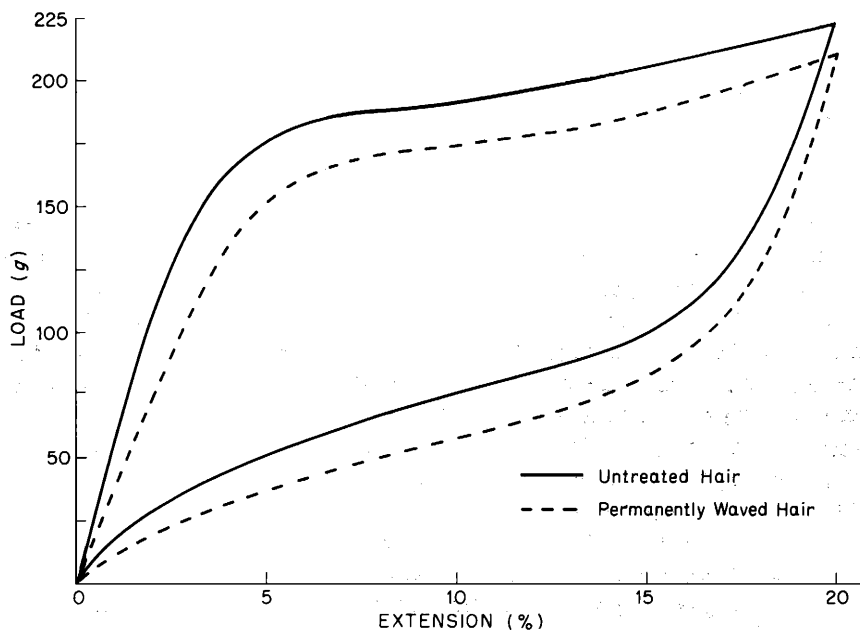


Figure 7.—Typical hysteresis curves for untreated human hair and permanently waved human hair.

allowed to contract again and is rested for a day. After a waving treatment, the hair is restretched. The load-elongation curves for the fibers before and after a waving treatment are shown in Fig. 7. The 20 per cent Index is calculated from the ratio of the areas under the curves and is taken as a measure of the effect of the waving process. A low value means that damage was done during the waving process. Naturally, the same test can be used to measure the effect of any other type of treatment of hair, such as bleaching or hair dyeing.

The machine is also used to study stress-relaxation. The hair is stretched 20 per cent at 85 per cent relative humidity, and kept there for ten minutes. The effect of various reagents on the hair can then be measured. The effects of mineral oil, water and waving lotion are shown in Fig. 8. Mineral oil has no extra effect on the hair. Addition of water, however, allows the stress in the hair to decay as links within the fiber, due to hydrogen bonds and salt links, are broken. The waving lotion produces even more dramatic effects. These curves are suited for mathematical analysis and, according to work in progress, the relaxation in a waving lotion (like ancient Gaul) can be split mathematically into three parts: that due to water, that due to the pH and that due to the mercaptan concentration.

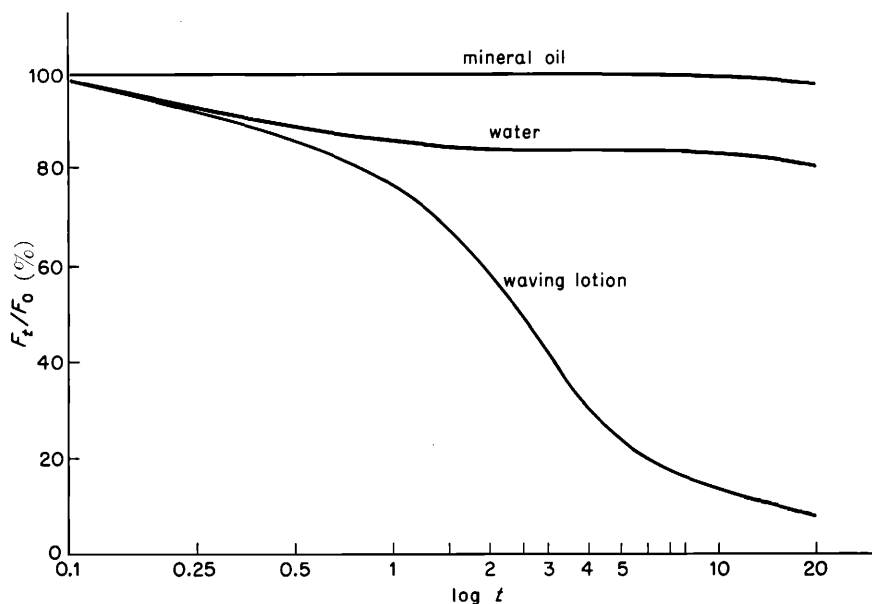


Figure 8.—Stress-relaxation curves for human hair treated with mineral oil, water and waving lotion.

## TGA AND DTA METHODS

Two instrumental methods that will probably see increased use in the cosmetic industry are those of thermogravimetric analysis (TGA) and differential thermal analysis (DTA). In the first method, the weight of a sample is continuously recorded as the temperature is increased. In the second, the temperature of a sample in a heating block is continuously recorded as the block temperature is gradually increased. The temperature is not identical with that of the block, as endothermic or exothermic reactions often occur at increased temperatures resulting in appreciable negative or positive temperature differentials.

Figure 9 shows how the TGA of sodium perborate tetrahydrate can be used to obtain information about the ease of loss of water of hydration and of its decomposition. Other cosmetic chemicals where similar heat stability problems are involved should prove amenable to this kind of treatment.

The DTA method is not concerned directly with weight changes but only in physical and chemical changes that involve heat loss or gain. Therefore, phase changes are observed as easily as decarboxylations. A comparison of TGA and DTA curves is a powerful method, since physical changes can then be distinguished from chemical changes such as are involved in oxidations and decompositions.

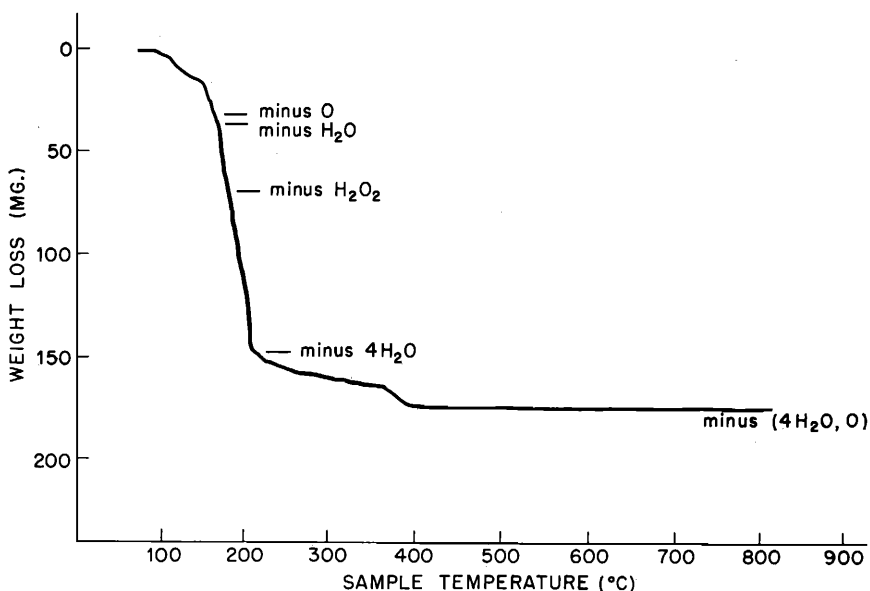


Figure 9.—Thermogravimetric analysis of sodium perborate tetrahydrate. Sample weight, 316.6 mg.

The sensitivity of the DTA method was shown by its ability to distinguish virgin hair from neutralized waved hair, from no-neutralized waved hair, from reduced hair. Figures 10 and 11 show the DTA curves given by these substances. The differences were not huge, by any means, and were complicated by the fact that even differences in the source of virgin hair were detectable, but the curves did indicate that real differences could be found.

#### OTHER POSSIBLE METHODS

There are many other instrumental techniques where increased use in cosmetics research can be foreseen. These range from mere extensions of those discussed, as for example electrochromatography where an electrical dimension has been added to paper chromatography causing the sideways migration of ionic species to be superimposed on their downward movement, to new excursions into the electronic realm of radio and microwave spectroscopy. The new methods of Nuclear Magnetic Resonance and Paramagnetic Resonance appear to have great potential as analytical tools.

If research money becomes more plentiful, the cosmetic industry will be able to acquire much greater benefit from the use of the electron microscope, the mass spectrometer, x-ray diffraction, etc. The electron microscope, especially, has proved invaluable in fiber research (7). It also played an important role in demonstrating the effectiveness of stannous fluoride as a protective treatment in preventing acid attack on tooth enamel (8).

Finally, we may speculate that the measurement of smells and odors may

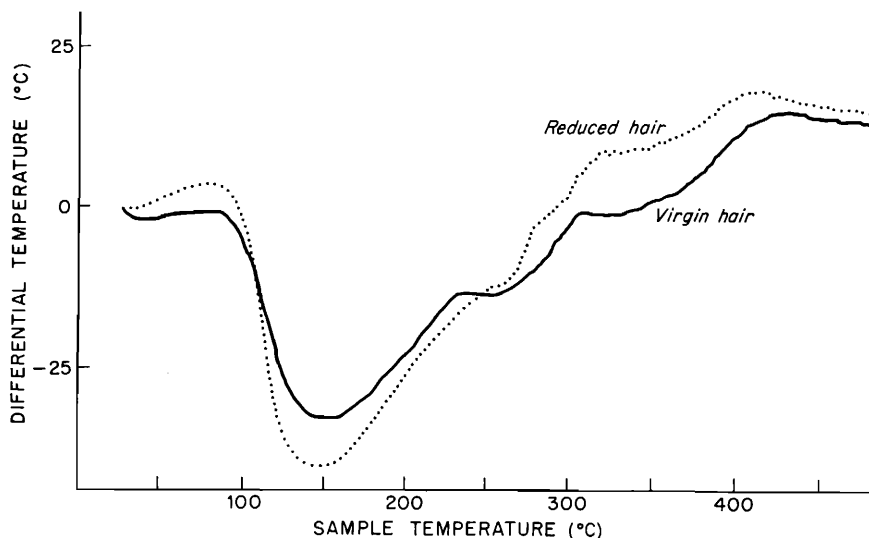


Figure 10.—Differential thermal analysis curves of reduced human hair and virgin human hair.

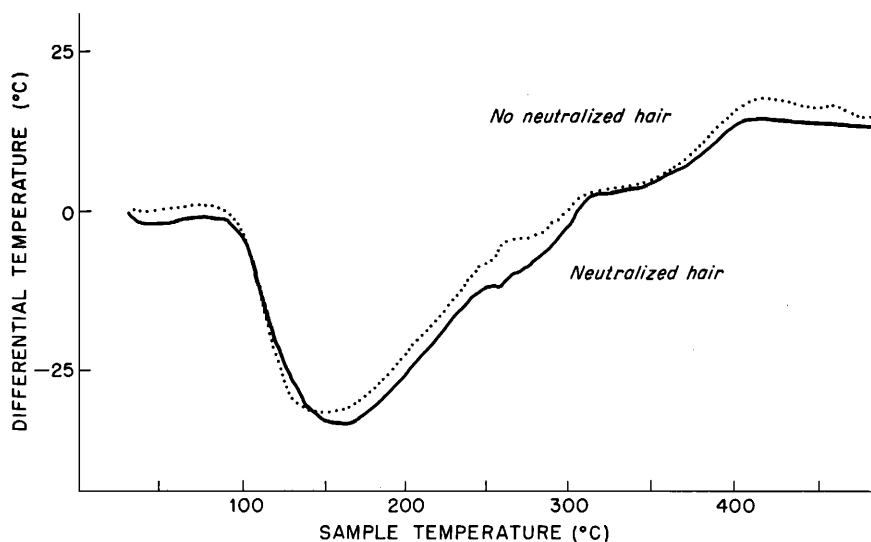


Figure 11.—Differential thermal analysis curves of human hair processed by “no-neutralizer” waving procedure and human hair after reduction and fixative treatment.

be achieved by instrumental means. This is a field that interests us a great deal, and we are confident that its application to problems in cosmetic research will eventually be achieved. The potential for such a method would seem to be enormous. The goal is well worth attaining.

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