

GENERAL DISCUSSION

MR. H. M. SMITH.¹—One spectroscopic method has not been considered today. I would be pleased if Mr. Rosenbaum would discuss the application of Raman spectra.

MR. E. J. ROSENBAUM.²—The difference between Raman and infrared is a difference in physical processes. Raman depends on modified scattering; infrared depends on absorption.

The basis of the modified scattering is closely tied up with the absence of absorption. In other words, if you have a sample that absorbs the exciting radiation even moderately, there will be essentially no Raman spectrum. If you are using the mercury 4358Å line, the blue line of the mercury arc, as most people do, any color in the sample is highly undesirable because it means that the energy is not going into scattering; it is going into absorption. If it goes into absorption, there is a possibility that the energy will be emitted as fluorescence. Then it will probably be stronger than the relatively weak Raman radiation, and what you are interested in will be completely blotted out.

Any observations of this type must be limited to samples that are essentially colorless and are not fluorescent. That, of course, is a real limitation when one is working in the higher molecular weight range. I think that

most of the work using this technique has been done in the gasoline range where this matter of color and fluorescence of the sample itself, as compared with incidental contaminants, is not so important.

In working with saturate fractions you can get water-white samples and under those circumstances you can get Raman spectra that have some use. Certain workers, notably those in Europe, have done some pretty good work along this line. Luther, in Germany, has published several interesting papers on the application of Raman spectroscopy to what we are discussing here.

The amount of fluorescence that can be tolerated depends on the quality of the apparatus that is used for the observation. Up to now I would say all Raman apparatus has been very much on the crude side. The one new element in the situation that I know of is an instrument that has been designed by Howard Cary and is just about to be supplied on a commercial basis. This instrument makes use of a double monochromator, which means that the radiation is first dispersed into a spectrum and a selected portion of that passes through an intermediate slit and is further dispersed in a second spectrometer.

If there is stray radiation from general scattering, or if there is continuous radiation from fluorescence, that will have a much smaller interfering effect

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² Sun Oil Co., Marcus Hook, Pa.

on the final result than with the use of a single monochromator. It would be my guess that the Cary instrument will represent a substantial improvement in the capability of Raman spectroscopy.

A MEMBER.—Since hot material is generally less fluorescent than material at room temperature, why is fluorescence not reduced by sampling the hot material?

MR. ROSENBAUM.—I do not think the effect on fluorescence is very great. At some stage you run into a situation in which the materials you are interested in are themselves fluorescent. There, I would say that the method just does not fit; it is out of the picture and one should use some other technique.

A MEMBER.—I talked to Mr. Luther and he has had good success by using higher temperatures to cut down this fluorescence and he goes up in wavelength of the exciting line. He operates with the yellow line and that has helped quite a bit.

MR. ROSENBAUM.—It does help a lot. However, experimental details become worse as you go to longer wavelengths. Scattering varies inversely as the fourth power of the wavelength. The detectors become less sensitive as you go to longer wavelengths. It is possible to do that, but that raises a question as to whether it is worth doing—whether the information you get that way is worthwhile. That is still a question.

MR. S. S. KURTZ, JR.³—I think if you are doing a lot of work in the lower molecular weight range it is very valuable, but not for lubricating oils.

MR. SMITH.—The subject of molecular sieves has not been discussed.

Is anybody here familiar with molecular sieves?

MR. S. GROENNINGS.⁴—At the American Chemical Soc. meeting in Atlantic City in September 1956 a paper was presented by H. Nelson of the Phillips Petroleum Co. on the determination of normal paraffins by molecular sieves. One of my colleagues, present at that meeting, mentioned that at Shell Development Co. we have been using essentially the same method and that we can extend its scope well into the 30-carbon atom range. The data obtained are usually 5 per cent low (basis true values). The principle of the method is that, owing to the precise structure of Linde's synthetic Zeolites, molecules up to 5 Å wide, covering all normal paraffins regardless of molecular length, will be retained in the pores, whereas wider molecules (isoparaffins, naphthenes and aromatics) will not. This method is more reliable than the urea method for determination and removal of normal paraffins in a petroleum distillate.

MR. F. W. MELPOLDER.⁵—We have looked into this a little and also have discussed it with others. It is believed that a high molecular weight straight chain compound enters the cage-like molecular sieve and curls around inside, dragging the rest of the chain through the opening. Once inside, the molecule is trapped and cannot easily be withdrawn from the sieve with eluting solvents.

Although the molecular sieve is useful for removal of straight chain compounds from a mixture, it is not recommended for compositional studies when one wishes to recover the sorbed material for subsequent analysis.

MR. G. G. RUMBERGER.⁶—This

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⁴ Shell Development Co., Emeryville, Calif.

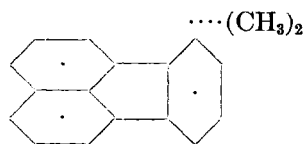
⁵ The Atlantic Refining Co., Philadelphia, Pa.

⁶ Marathon Corp., Menasha, Wis.

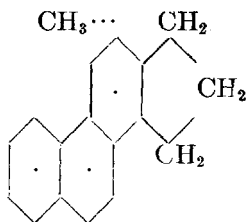
method might solve some of the problems in doing further analysis on reactive material. There is a problem of differentiation between reactive materials which are normal paraffins and those which have some side branching.

MR. E. G. CARLSON.⁷—We have used this technique in analyzing wax. It is a handy way to remove the large quantities of normal alkanes when one is interested in taking a look at the

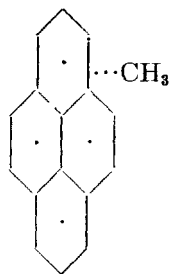
the difference in basicity of different classes of polycyclic aromatics which have otherwise very similar properties, that is, vapor pressure, adsorption coefficient, etc., can be used to advantage in obtaining one further stage of separation. Recently we produced fractions by fractional distillation of a catalytically cracked oil and a rather exhaustive chromatography, which still contained the following types of aromatics:



Fluoranthene



Cyclopentenophenanthrene



Pyrene

NOTE.—Position of methyl groups not established.

nonnormal alkane components by methods such as mass spectrometry.

Experimentally, the removal of normal alkanes by the sieve is readily carried out. We dissolve the wax in an appropriate solvent and contact it batchwise with sieve. The normal alkanes can be essentially all removed in one batch since they readily enter the sieve but desorb with great difficulty.

MR. SMITH.—The Kettering Laboratory in Cincinnati has done a lot of work on polycyclic aromatics. They use certain methods of separating them in addition to the techniques discussed in the formal papers. I would like Mr. Horton of the laboratory to give us a few words of some of their experiences on polycyclic aromatics.

MR. A. W. HORTON.⁸—Sometimes

At temperatures of about 0 C, these compounds may be exposed to concentrated sulfuric acid for a brief time without sulfonation. Apparently, the pyrenes are significantly more basic than the other two classes since they may be extracted from the above mixture fairly cleanly by partition between isooctane and concentrated sulfuric acid at 0 to 5 C. The pyrenes dissolve in the acid without sulfonating and upon dilution of the acid phase with ice they may be recovered unchanged.

One other technique which has not been discussed here is that of the formation of complexes with maleic anhydride. This compound is most useful in obtaining separations of anthracenes from phenanthrenes (and similarly benzantracenes from chrysenes and pyrenes). The complexes are formed by refluxing the oil together with a high ratio of maleic anhydride in benzene solution for 16 to 24 hr.

⁷ Shell Oil Co., Inc., Houston Research Laboratory, Houston, Tex.

⁸ Kettering Laboratory, University of Cincinnati, Cincinnati, Ohio.

Separation of the complex from the unreacted material is accomplished by hydrolyzing the anhydride to the sodium salt of a dicarboxylic acid, separating the aqueous phase from the oil, acidifying, and extracting the acid complex with an organic solvent. The original hydrocarbons, either the anthracenes or the benzantracenes, are then regenerated from the complex by heating it rapidly in a mixture with soda lime and collecting the distilled hydrocarbon on a cold wall.

MR. E. L. DERR.⁹—I understand that in the effect of the biological activity of this polyaromatic that until you get to a side-chain of the same carbon number as the nucleus itself you get only slight increase in this activity. What happens if this side-chain is extended 2 or 3 carbons? Does it still maintain this high activity or does it drop off again? If it drops off again it looks, of course, like a specific biological effect. If it seems to improve as it goes beyond this level, it could be due to an absorption effect where you are improving the solubility behavior of this compound as a result of increased alkylation.

I would like to mention one thing concerning the separation of the various structures of polyaromatics with isooctane and sulfuric acid. You will probably find that HF - isooctane would furnish still better separation because such segregation is probably due to acid-base characteristics of the aromatics. For instance, you can separate phenanthrene and anthracene very favorably this way. As shown in a recent paper by E. L. Mackor *et al*¹⁰, these separations can be related to the interaction of the electrons in the aromatic nucleus with the proton of the strong acid. This does not have

a bearing on the solvent picture we presented in our paper¹¹ which would not allow us to distinguish between these minor structure differences.

MR. KURTZ.—If we can determine carbon type composition of viscous oils easily by physical property correlations, and if we can determine aromatic ring types by ultraviolet spectroscopy, is there much real need for other information on viscous oils?

I am serious about this. I think that we can, as a group of petroleum chemists, afford to get a great deal of information about the composition of petroleum. I hope the work API Project 6 is doing is continued for a long time and that they get a very complete story on the composition of petroleum.

From the ASTM point of view, we are just about at the point where we think we may want to do something about correlations and analytical methods for viscous fractions of petroleum. If we can standardize on an approach to carbon type correlations that give you per cent C_A , per cent C_N and per cent C_P we can get something that we can agree on. Our work has indicated that there are a variety of ways that are equivalent; therefore, we should pick out one that is easy to use.

I think it is also worthwhile for us to get something worked up that is fairly simple and could be used to determine the aromatic ring types. If you make a separation of aromatics by gel, you get an aromatic concentrate. I think it is feasible and desirable to get the monocyclic, bicyclic, tricyclic that are present, probably by ultraviolet. I think this is a reasonable target for ASTM Research Division IV of Committee D-2 to aim for.

MR. B. A. ORKIN.¹²—While the

⁹ Shell Development Co., Emeryville, Calif.

¹⁰ E. L. Mackor, A. Hofstra, and van der Waals, "The Basicity of Aromatic Hydrocarbons," *Transactions of the Faraday Society* Vol. 54, No. 66 (1958).

¹¹ See p. 111, this symposium.

¹² Socony Mobile Oil Co., Inc., Paulsboro, N. J.

physical properties of lubricating oil are very important, I think most of us are aware that the chemical properties cannot be overlooked. There is oxidation.

While we may make lubricating oils with desirable physical properties, they are not much good if they are unstable. There are also such things in the oils that people for years have been calling inhibitors, and we would like to know what they are.

Until we can tear them apart, we are a long way off, and ring analyses will not help us a bit. They do not help us to identify very small individual groups or individual types. Those are things that will compel research people to look for better instruments and methods, for better methods of separation and identification. The ring analyses only give us averages.

MR. G. S. JAFFE.¹³—I have heard little mention of any nitrogen compounds in the discussions so far. These polar compounds increase in importance as we look at more viscous oils. So by studying only the aromatic ring systems and avoiding the analysis of materials less readily eluted from silica gel, we are overlooking an important part.

MR. DERR.—As long as the heteroatom concentration is not too severe, I think we can assume the molecules will distribute solution-wise in accordance with their hydrocarbon skeleton. In the heavy residues, where there may be large amounts of nitrogen or sulfur, we are not in a position to say.

¹³ Shell Development Co., Emeryville, Calif.