INFRARED CHEMICAL ANALYSIS: A NEW APPROACH

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Utilizing an unusual low temperature sampling technique, a new approach to infrared chemical analysis which exhibits micromole sensitivities has been developed. The principal attribute of this new approach is that it offers a very general method for gas mixture analysis; a method which requires no previous knowledge of mixture composition and which entails no preanalytical separation of classes of components. Mixtures containing alkanes, alkenes, aldehydes, ketones, ethers, inorganics and aromatics may be at least qualitatively analyzed by a single step spectrophotometric procedure. Because this new approach to infrared analysis offers a very general method for determining the components of gas mixtures, it should find application in the fuel industry as a tool for kinetic and mechanistic studies of chemical combustion and as an aid in the study of combustion intermediates. This area of research is taking on increasing immediacy as we become more sensitive to the ecological menace posed by air pollution.

Sample preparation consists of diluting the gas mixture to be analyzed with a large excess (usually at least 100 fold) of nitrogen followed by condensation of the diluted gas mixture in pulsed fashion onto an infrared transmitting window previously cooled to 20°K. Using semiautomated procedures, sample preparation and deposition may be completed in less than one minute. A standard double beam spectrophotometer is used for recording the spectral data although enhanced analytical sensitivity may be obtained with modified instruments. The time required for recording a suitable spectrum varies with the problem in hand. Exhaustive analysis of an unknown mixture would, of course, require more time than would a search for some specified set of mixture components.

In the May issue of Analytical Chemistry, this technique of low temperature infrared matrix dispersion analysis is described and application of the technique to the analysis of a series of thirteen simple hydrocarbons is reported (Rochkind, M. M. (1967)). Since that writing, an additional fifty gases and volatile liquids have been examined (see, Table I), and we are now in a position to make concrete remarks regarding the analytical potential of this technique as it is applied to a broad range of chemical compounds. This will be done at the Symposium. In addition to discussing actual performance of this technique as an analytical tool, the equipment requirements will be outlined and some attention will be paid to the adaptation of automated methods with regard to sample preparation and sample deposition.

Table I. Gases and Volatile Liquids for which Standard Spectra Have Been Recorded

ALKENES

Allene
Butadiene
1-Butene
cis-Butene
trans-Butene
2,3-Dimethyl-2-Butene
Ethylene
3-Ethyl-1-Pentene
3-Ethyl-2-Pentene
Isobutylene
3-Methyl-1-Butene
2-Methyl-2-Butene
2-Methyl-1-Pentene
4-Methyl-1-Pentene
trans-4-Methyl-2-Pentene
1-Octene
1-Pentene
Propylene
2,4,4-Trimethyl-1-Pentene

ALKYNES

Acetylene
Ethyl Acetylene
Methyl Acetylene

ALDEHYDES

Acetaldehyde
Propionaldehyde

ETHERS

n-Butyl Ethyl Ether
tert-Butyl Ethyl Ether
Dimethyl Ether
Ethyl Ether
n-Propyl Ether
Vinyl Ethyl Ether

AROMATICS

Benzene

ALKANES

Butane
Cyclopropane
2,4-Dimethylpentane
Dimethyl Propane
Ethane
Heptane
Hexane
Isobutane
Isopentane
Methane
Octane
Pentane
Propane
2,2,5-Trimethylhexane
2,4,4-Trimethylpentane

KETONES

Diethyl Ketone
Dimethyl Ketone
Dipropyl Ketone
Ethyl Butyl Ketone
Ethyl Propyl Ketone
Methyl Butyl Ketone
Methyl Ethyl Ketone
Methyl Isobutyl Ketone
Methyl Pentyl Ketone
Methyl Propyl Ketone

INORGANICS

Ammonia
Carbon Monoxide
Carbonyl Sulfide
Hydrogen Sulfide
Sulfur Dioxide
Water

Different levels of sophistication may be pursued in connection with analysis of the raw spectral data. These range from hand analysis, using specially prepared tables, to strictly computer controlled analyses where the raw spectral data are digitized, transmitted over telephone lines to some centrally located computer facility and analyzed within the computer. An intermediate level of sophistication, one manifestly practical, involves transmitting via teletype a list of frequencies and approximate relative intensities to a central computer at some remote location within which analysis of the relevant data is performed. While the latter approach obviates digitization of the raw spectra, it poses the requirement that competent personnel must be present at the site of the experiment to reduce the spectral graphs to a list of meaningful frequencies and relative intensities. This level of sophistication, though less efficient on an absolute scale than a strictly computer controlled analysis, is very much easier to effect and suggests some exciting possibilities which utilize the time sharing capabilities of new generation computers. The paper to be presented will discuss this data handling problem in detail from the points of view of communications, equipment requirements, cost analysis and effectiveness. Computer controlled microfilm facilities for storing spectral data - where intelligible data need to be retained in an available state - will be discussed as well.

As pointed out in the May issue of Environmental Science and Technology, this method of infrared chemical analysis is strikingly computer oriented (Rochkind, M. M. (1967)). This is so because the sampling technique results in narrow bands (2-6 cm^{-1} bandwidths) which occur at well distributed frequencies, reproducibly from sample to distinct sample. It thus is possible to completely characterize a chemical species by a short list of frequencies (and, perhaps, relative intensities), each accurate to 1-2 cm^{-1}. This greatly simplifies the data handling and the data storing problems.

It appears as though solids may also be susceptible to the kind of matrix dispersion analysis described above for gases. A proposal for preparing samples from solid material which employs pulsed lasers and molecular beams will be considered and some possible attendant problems will be discussed. Relatively nonvolatile liquids (i.e., those having vapor pressures of less than 1 torr at room temperatures) present yet more difficult problems, but even these may be surmounted if need be.

In summary, it appears as though low temperature matrix dispersion - a technique whereby gaseous materials are sufficiently dispersed (not isolated) that in the solid state they exist in a quasi-homogeneous environment within which molecular interactions are minimized - provides a practical technique for

sample preparation and permits a new approach to infrared chemical analysis. Work is currently underway to define precisely the quantitative capabilities of the method. Progress in this area will be briefly reported.

References Cited

1. Rochkind, M. M., Anal. Chem. 39, 567 (1967).

2. Rochkind, M. M., Environ. Sci. Technol. 1, 434 (1967).

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