Dept. of the Navy

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Title: The Use of Ionization Methods in Determination of Atmospheric Impurities

/K voprosu o primenenii ionizatsionnykh metodov pri opredelenii atmosfernykh zagryazneniy/

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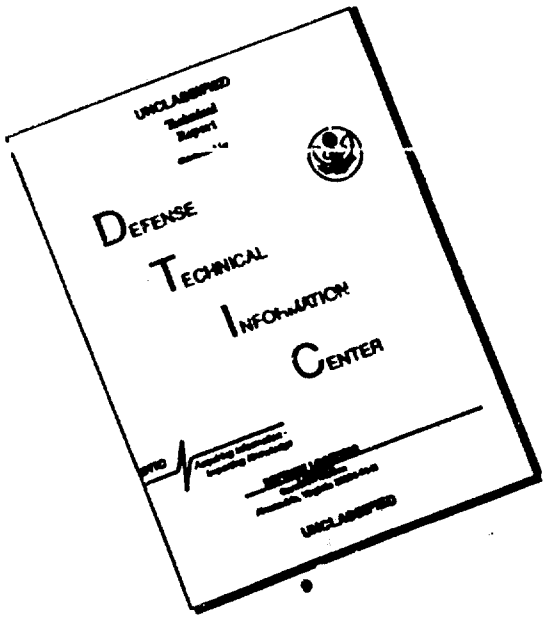

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The essential feature of ionization methods based upon the use of matter in its plasma-like state is the fact that during physicochemical analysis of the air, are transformed into determinable gaseous ions which can then be identified and measured by electronic computers. Concentrations of ions and small ion currents are widely determined in modern instrument-building, and calculations are even being conducted of separate ions. Ionization methods, thanks to the use of appropriate radioelectronic means, have considerable advantages over the usual means of chemical analysis. They assure uniformity and precision of measurement, rapidity of determination and automatic registration of the results received.

In research on the atmosphere, the basic physicochemical parameters of the air: its composition, density and humidity, and atmospheric pressure, are being most precisely established with the aid of ionization methods, and about 30 various meteorological elements are being studied (M.T. DMITRIYEV). These methods are being used widely in scientific work and technology (Cadle). In connection with their forthcoming widespread introduction into sanitary-hygienic practice in the not-too-distant future, it will not be without interest to examine the theoretical bases of, to conduct appropriate experiments on, and to note the prospects for, the use of ionization methods in uncovering atmospheric impurities.

The most natural subdivision of ionization methods is perhaps the one brought about by the energy level of ionization and the means of gaseous ion formation. In particular, the following methods are of interest for atmospheric chemistry: The thermoionization, photoionization, electric discharge, radioactive ionization, argon-ionization, electron-capture, and the mass-spectrometric methods. The peculiarity of the thermoionization method is the fact that the ionization of gasses is conducted thermically, by means of heating. The flame-ionization method, in which thermal ionization takes place in a hydrogen flame, is the one that has received most widespread distribution in practice. Temperature of the hydrogen flame does not exceed 2,200°, which corresponds to an ionization energy level of 0.2 ev. A thermionic method is also used for chemical analysis, in which thermal ionization is accomplished on a surface, for example, in evaporating ions of lithium. The temperature of surface ionization is about 700° which corresponds to a level of ionization of only 0.1 ev.

In the photoionization method, ionization of the molecules is carried out by optical radiation. Since the threshhold of ultraviolet radiation is taken as equal to 10 mm., the level of photoionization thus amounts to 125 ev, which considerably exceeds the potentials of molecule ionization (<24 ev). In photoionization within the visible spectrum (above 4,000 A) the level of ionization amounts to 3.1 ev., which is insufficient for obtaining the requisite high concentrations of ions. With the use of quartz discharging lamps, the level of ionization amounts to 7 e.v. (over 1,800 A), which permits determination of only multiatomic molecules. The use of the photoionization method, which requires powerful sources of optical radiation, is fraught with experimental difficulties. The electric-discharge method is one in which ionization of molecules is attained by means of the energy of an electric field. Due to the properties of the spontaneous gaseous discharges utilized in this method (silence, decaying, crowning and high-frequency), the level of ionization which the electrons (in the main) and ions produce exceeds by only several electron-volts the potential of ionization of the gasses in the discharge interval, i.e., amounts to 15-25 ev.

The radioactive ionization method, as it is called, is one in which the ionization of molecules is accomplished by means of ionizing radiation -- α- and β particles. With a constant environment of gas, temperature, and pressure in the ionization chamber, the current passing through it is also kept constant. If there are impurities in the air, then due to the difference in probabilities of ionization the stream of ions in the ionization chamber is essentially changed. The level of ionization is determined by the energy of radioactive radiation and considerably exceeds the energy of ionization of the molecule. In the argon-ionization method ionization of the molecule is carried out by the agitated organ atoms. The agitated atoms of argon will be formed under the action of radioactive radiation somewhat earlier than argon together with the components to be determined, and will fall into the area of a measurable ion stream. If there are foreign molecules present in the agitated argon, then the excitation energy is transferred into kinetic energy of the admixture's valent electrons, as a result of which they undergo ionization (in collisions of the second kind as distinct from collisions of those of the first kind in the radioactive ionization method, in which the ionization is accomplished by means of the kinetic energy of fast particles). Because the excitation energy of argon atoms is 11.6 ev., molecules whose excitation energy exceed this value will not form ions and, consequently, are determined according to the change in the ion stream. Thus the level of ionization with the argon-ionization method

is 11.6 ev. Helium may be used instead of argon: the level of ionization by agitated atoms in this case is considerably greater, which permits analysis of any kind of matter except neon. However, the sensitivity of the method is considerably reduced with this.

The essence of the electron-capture method consists in the fact that the molecules of impurities are ionized by the capture of electrons and are transformed into negative ions. The process of electron capture (adhesion) itself requires minimal energies--about 0.1 e.v., however, it is impossible to determine impurities by this method without ionization of the basic carrier-gas, which serves as the source of free electrons. Ionization is usually carried out by radioactive radiation of great energy, exceeding the ionization energy of the molecule. And finally, in the mass-spectrometric method, ionization is usually carried out by electrons accelerated in an electric field. Radioactive radiations and electric discharges also are used for ionization. The peculiarity of this method is that the ions are divided according to their masses; this tremendously simplifies identification of the impurities under investigation. Division of the ions of various compounds is achieved in electric, as well as magnetic fields. Because of the capability of calculating separate ions of various mass numbers, this method is the most sensitive one.

The comparative characteristics of the various ionization methods are given in the table. The thermo ionization method has sufficiently high sensitivity, but permits analysis only of organic molecules. The photoionization methods have higher sensitivity, but due to practical difficulties are suitable only for multiatomic molecules with low ionization potential. The sensitivity of determining by this method, the oxygen and haloid-containing compounds, which hinder

CHARACTERISTICS OF IONIZATION METHODS

	Degree of ionization (in %)	Level of ionization in ev	Max sensitivity (in MKG)	Compounds that can be determined	Required Vol Air (in CM^3)	
					At 10^{-4}	10^{-5}
Thermoionization	$1-3\ 10^{-3}$	0.1-0.2	10^{-6}	Organic	10	100
Photoionization	0.05	7-125	10^{-7}	Multi-atomic	1	100
electric-discharge	0.5	15-20	10^{-8}	any	0.1	10
argon-ionization	1-5	11.6	10^{-7}	Multi-atomic	1	100
electron-capture	2-4	>25	10^{-8}	Oxygen-and Haloid-containing	0.1	10
Mass spectrometric	0.1	1-200	$<10^{-8}$	any	<0.1	<10

ions from collecting, is 10^3 - 10^4 times lower. The electric-discharge method has high sensitivity, including sensitivity toward organic compounds as well, and is suitable for determining any gaseous compounds. But it is not very satisfactory because of the instability of the discharge processes and instability of the ionization thus being created. The radioactive ionization method is suitable for determining all compounds without exception, but has relatively lower sensitivity in comparison with other ionization methods. The argon-ionization method has good sensitivity (due to the high degree of ionization), but permits analysis only of multiatomic compounds (whose ionization energy are below 11.6 e.v.). The electron-capture method has high sensitivity, but is suitable only for oxygen and haloid-containing compounds and certain other materials which have polar-functional groups in their makeup. The mass-spectrometric method is the most universal, although it is also the most complex (relatively bulky apparatus is required, and a vacuum is needed for the instruments to operate).

As is apparent from the table, the maximal sensitivity of the ionization methods, depending upon the level and degree of the means of ionization, amounts to 10^{-8} - 10^{-6} mkg., i.e., more than 10^5 - 10^6 times higher than the sensitivity of the photo colorimetric, polarographic and spectral methods, and more than 10^{10} times higher than the sensitivity of chemical methods of weight and volume analysis. Of other physico-chemical methods, only the radioactivation method (in which the materials to be determined are transformed into traceable radioactive molecules) is comparable in sensitivity to the ionization methods, or even exceeds them.

It is apparent from the table, moreover, that the sensitivity of the ionization methods grows with the increase in degree of ionization of the molecules to be determined (which on the whole is conditioned by the means of ion formations). With an increase in the level of ionization up to the values of ionization energy of the molecules (10-20 e.v.), the sensitivity of the methods is also increased. In view of its high sensitivity, a considerable degree of ionization is not compulsory for the mass-spectrometric method.

Concentrations of atmospheric impurities of about 10^{-4} mg/m^3 are assumed to be the minimal limit of those worked out by Soviet hygienists. As is apparent from the table, air samples of only 1-10 cm^3 in all, are necessary for determining impurities in such concentrations, i.e., the usual medical syringes can be used. With concentrations of 10^{-6} mg/m^3 (1% of the established minimal PDK), which also must be measured in order to control the cleanliness of the air, sample volumes which do not exceed one l (i.e., a volume

which can be put into the instrument entirely) are needed for the analysis. This indicates that, with the aid of the ionization methods, air can be put directly into the instrument without first being enriched with other compounds.

Thus, all of the ionization methods of physicochemical analysis examined above can be used successfully for determining atmospheric impurities. As examples, several chromatograms and mass-spectrograms (registers of peaks in relation to times) are given in figures 1 and 2. Figure 1a shows the dependence of voltage (proportional to the ionizing current, registered by means of a recorder) when using the argon-ionization method, and in fig. 1б--the same when the thermoionization method is used (chromatograms). Before putting the sample we have determined into the ionizing instrument, it is passed through a gas-chromatographic column of 5 mm in diameter which is filled with an adsorbent-carrier.

In the case of determining a mixture of lead tetraethyl (see fig. 1a) with a surplus of isooctane the column was filled with a silicon lubricant (3% on Inzenskiy brick). As indicated on the diagram, isooctane (first peak) began to enter the area of ionization within 1 min after the sample entered the column, but lead tetraethyl--in the 9th minute.

In the case of determining tetrahydrofuran (see fig. 1б) with a surplus of oxygen, the column was filled with dibutyl phthalate (25% on Inzenskiy brick). As indicated on the diagram, oxygen (first peak) began to enter the area of ionization (hydrogen flame) within 30 sec. after entering the gaseous mixture.

Tetrahydrofuran entered the area of ionization in the 6th minute (the oxygen peak in this diagram is negative, because its molecules did not increase but decreased the value of the ionization current. In the figure it is shown above the line for convenience of graphic illustration.

A mass-spectrogram of polluted air (register of voltage, in relation to times, proportional to the value of the ionization current) is shown in fig. 2. Obtained with this were peaks for acetaldehyde, acetone, crotonic aldehyde, tetrahydrofuran, hexane, dioxane, heptane, nitrobenzene, 4-chlorocarbon and m-nitrochlorbenzene. On the mass spectrogram the peaks are obtained in the increasing order of molecular weight (the first figure in parentheses), therefore the materials with the small mass numbers are written first on the tape.

Because pollution of the air took place as a result of the process of evaporation (the second figure in parentheses corresponds to the boiling temperature of the material at

atmospheric pressure), acetaldehyde was detected in the greatest quantity. Its concentration, roughly equal to 0.05 mg/e, we took as 100. The concentrations of the remaining materials were considerably lower (third figure in parentheses). The mass-spectrometric method enables us to identify atmospheric impurities (according to mass numbers) and simultaneously to determine their concentrations.

LITERATURE

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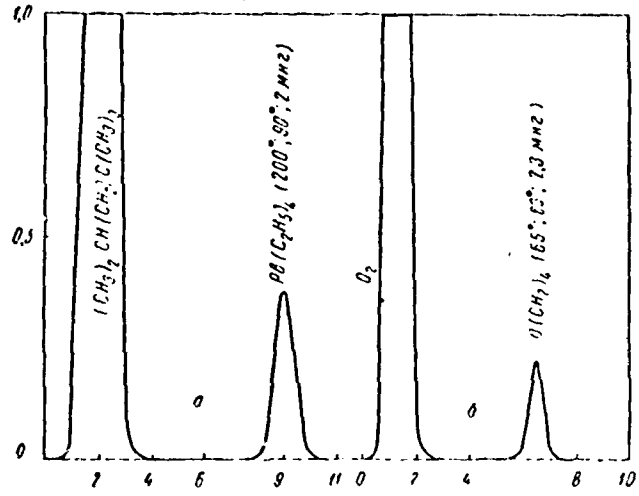

Figure 1. Dependence of Voltage on time (chromatograms, registered by means of a recorder). On the ordinal axis--voltage (in mv), on the abscissa axis--time (in min.): a-division of lead tetraethyl in a mixture with a surplus of isooctane, registered by the argon-ionization method; b-division of tetrahydrofuran in a mixture with a surplus of oxygen (in the air), registered by the thermoionization method. Figures in parentheses after the formulas correspond to: boiling temperature of the material at atmospheric pressure; the detected amount of impurities (in mgk). Further explanation in the text.

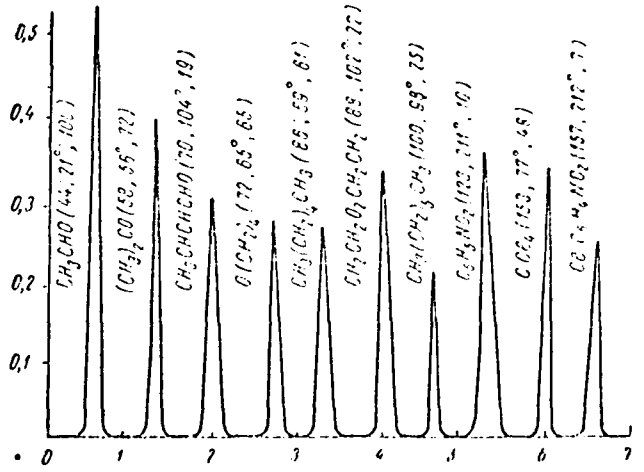

Figure 2. Dependence of Voltage on Time (Mass-spectrogram, registered with the aid of a recorder)

On the ordinal axis--voltage (in mv), on the bascissa--time (in min). Figures in parentheses after the formulas correspond to: molecular weight of the material; boiling temperature at atmospheric pressure; concentration in the air (in relative units).