INSTRUMENTS AND METHODS OF INVESTIGATION

The Lindinger device detects products of physiological processes

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Fine physical methods can form the basis of contemporary measuring equipment providing qualitatively new possibilities for the analysis of processes and phenomena in various fields of science. Below we briefly describe the Lindinger device [1, 2], which allows one to measure the content of some molecular admixtures to gases if their concentration is as low as 1 ppb (10^{-9}) . Central to this device is the flow measurement of the rate constants for various ion-molecule processes. This method goes back to the 50's-60's, when quadrupole mass-spectrometers were designed. The scheme of the apparatus is shown in Fig. 1. Certain ions are inserted into a flow of a buffer gas with some admixture of known concentration. While the gas flows inside the device the ion-molecule processes proceed between these ions and admixed molecules, so that ions of a new sort are produced. Currents of these and primary ions are measured by a quadrupole mass-spectrometer at the output of the device. The number density N_i of the ions formed is determined by the balance equation

$$\frac{\mathrm{d}N_i}{\mathrm{d}t} = kN_i'N,\tag{1}$$

where k is the rate constant of this process, N'_i is the number density of primary ions, and N is the number density of admixed molecules. In the limit $N_i \ll N'_i$, the solution to this equation yields

$$\frac{N_i}{N_i'} = k N \tau \,, \tag{2}$$

where τ is the flow time. Note that in this limit, relationship (2) is independent of any other processes in the system. Hence, measuring the ratio between the initial and produced ion currents, one can find the rate constant of the process if the number density of admixed molecules is known. This technique was used in many laboratories to measure the rate constants of various ion-molecule processes (for example, the reader is referred to Ref. [3] containing valuable data on the rate constants of many ion-molecule processes, which were obtained by this approach in the 60's).

The Lindinger device deals with the inverse problem with respect to the measurement of rate constants. If the rate constant of a certain process is known, one can determine the

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Figure 1. A scheme of the drift-flow method: 1 — flow of a buffer gas with an admixture; 2 — entrance of H_3O^+ ions into a gaseous flow; 3 — exit of the main flow; 4 — drift tube; 5 — condensed ion lenses; 6 — quadrupole mass spectrometer; 7 — ion collector.

admixture concentration by the above measurement and formula (2), the measured concentration being of the order of 1 ppb (10^{-9}) . In the Lindinger device H_3O^+ (or $H^+ \cdot H_2O^+$) ions are used as the primary ones. The possibility for these ions to take partin reactions with some molecules is determined by the proton affinities of the molecules as compared to those of water molecules. The values of the proton affinities are listed in Table 1. If the proton affinity of a given molecule is noticeably lower than that of a water molecule, which is 7.2 eV, the ion H_3O^+ does not interact with this molecule. Table 1 lists some atoms and molecules of this kind in the left column and these atoms and molecules can be used as a buffer gas. On the contrary, molecules with higher proton affinities can react with the H_3O^+ ion, i.e. the concentration of these species in a buffer gas can be measured. The data on these molecules are presented in the right column of Table 1.

Clearly, one can run into additional problems when measuring the amount of air admixtures. However, experience in the use of this technique enables them to be overcome. For example, in atmospheric air of moderate humidity $H_3O^+ \cdot H_2O$ ions can also be formed apart from H_3O^+ ions.

Table 1. Proton affinities (PA) of some atoms and molecules [2, 4].

| Atom, molecule | PA, eV | Atom, molecule | PA, eV |
|---|--|---|---|
| He Ne Ar Kr | 1.8 2.1 3.8 4.4 | C ₄ H ₁₀ H ₂ S HCN C ₆ H ₆ C ₂ H ₄ | 7.1 7.4 7.4 7.8 7.8 |
| $\begin{array}{c} \mathbf{R}_2\\ \mathbf{O}_2\\ \mathbf{N}_2\\ \mathbf{X}e\\ \mathbf{CO}_2\\ \mathbf{CH}_4\\ \mathbf{N}_2\mathbf{O}\\ \mathbf{CO}\end{array}$ | 4.4 4.4 5.1 5.1 5.7 5.7 5.9 6.2 | C ₃ H ₆ HCOOH CH ₃ OH CH ₃ CN CH ₃ COH C ₂ H ₅ OH CH ₃ COCH ₃ NH ₃ | 7.8 7.9 8.1 8.1 8.2 8.5 8.8 |

The use of a longitudinal external electric field enables one to reduce their concentration by increasing thir mean energy. Clearly, formulas (1) and (2) should take into account the rate constant and flow time, which are changed due to increased average ion energy and ion drift along the electric field, respectively.

The Lindinger device proved to be useful in measuring the concentrations of some products of physiological processes in atmospheric air. Its potentialities are illustrated in Fig. 2, which shows concentrations of some molecules in expired air. Being interested in the potentialities of the Lindinger device, we do not discuss here the dependence of the results on the experimental conditions or particular operators. Figure 3 presents another example of the device application, i.e. the time evolution of concentration for some products of meat degrodation. These examples prove the utility of the Lindinger device studies of various processes involving living organisms.

Along with the analysis of physiological processes, the Lindinger device is useful for aerophysical measurements. For example, tropospheric acetone and methane are generated partially as a result of biological processes in plants [5], and careful measurements of these species can provide a deep insight into the problem. The above facts together with the reliability and simple scheme of measurements show that the



Figure 2. The concentration of allyl methyl sulfide (a), dimethyl sulfide (b), and acetone (c) in expired air after the consumption of garlic [2].



Figure 3. The content of some components in air as a result of meat degradation at room temperatures [2].

Lindinger device will find application in the measurement of low molecular concentrations in buffer gases.

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