

# AIR IONS AND ELECTRICAL AEROSOL ANALYSIS

## Introduction

Natural air contains permanent gases ( $N_2$ ,  $O_2$ , Ar, Ne, He, Kr,  $H_2$ ,  $N_2O$ , Xe), and variable components ( $H_2O$ ,  $CO_2$ ,  $CH_4$ , CO,  $O_3$ ,  $NH_3$ , NO,  $NO_2$ ,  $SO_2$ ,  $H_2S$ , hydrocarbons, organic compounds containing oxygen, nitrogen, and sulphur, element-organic compounds, etc.) [1, 2]. The concentration  $c$  of unpermanent gases in the troposphere varies between traces ( $c < 1$  ng) to several microgrammes (in the case of  $H_2O$  to several grammes) in  $m^3$  [2, 3]. Biosphere is the largest source of organic emissions into the troposphere. These emissions include also pyridine bases, i.e. mixtures of heterocyclic organic compounds (pyridine, picolines, lutidines, collidines). Pyridine bases are formed also in combustion processes of fossil fuels, oil shales, turf, and in the incineration of wood and bone [4]. Mass-spectrometric measurements confirm their presence in natural air [5].

In addition to neutral molecular components the air also contains a certain amount of radicals O, OH,  $HO_2$ ,  $CH_3O_2$ , etc. ( $10^4$ - $10^9$  molecules in  $cm^3$ ), and air ions (small air ions of an order of  $10^2$ - $10^3$  pairs in  $cm^3$ ). Cosmic irradiation and radiation of radioactive compounds cause the formation of primary ions ( $N_2^+$ ,  $O_2^+$ ,  $H_2O^+$ ,  $CO_2^+$ ,  $O_2^-$ ,  $O^-$ ,  $OH^-$ , etc.) from neutral molecules. In ion-molecular reactions with molecules the primary ions are transformed into small air ions. The composition of the latter in the troposphere has not been finally established.

It is known that the mobility spectrum of small air ions is sensitive to a number of admixtures in the air [6, 7]. The difference between urban and rural spectra of positive small air ions [8] may be connected with the differences in the chemical composition of the air. Pyridine and its homologues may influence the composition of positive small air ions [5]. The present paper will consider the influence of pyridine, 2-picoline, 2,3-, 2,4-, 2,5-, 2,6-lutidine and  $\gamma$ -collidine on the mobility spectrum of small air ions.

### Objects and methods of the investigation

The objects of the investigation are ordinary urban air in a relatively clean laboratory of 50 m<sup>3</sup>, and admixtures: pyridine, methylpyridine, dimethylpyridines, trimethylpyridine. Table 1 presents certain physical-chemical properties of the latter and of NH<sub>3</sub> and H<sub>2</sub>O [9]. Water and ammonium have an important role in the formation of positive air ions [5].

Table 1  
Physical-chemical properties of some pyridines, NH<sub>3</sub>, and H<sub>2</sub>O

Compound	Formula	Molecular mass amu	Boiling point °C	Proton affinity eV
Pyridine	C <sub>5</sub> H <sub>5</sub> N	78	115.3	9.6
2-picoline	CH <sub>3</sub> C <sub>5</sub> H <sub>4</sub> N	93	128	9.75
2,4-lutidine	(CH <sub>3</sub> ) <sub>2</sub> C <sub>5</sub> H <sub>3</sub> N	107	157	9.83
2,6-lutidine	(CH <sub>3</sub> ) <sub>2</sub> C <sub>5</sub> H <sub>3</sub> N	107	143	9.83
γ-collidine	(CH <sub>3</sub> ) <sub>3</sub> C <sub>5</sub> H <sub>2</sub> N	121	172	10
Ammonium	NH <sub>3</sub>	17	-33.5	9.4
Water	H <sub>2</sub> O	18	100	7.3

In the laboratory room people worked only in the case of extreme necessity (adjustment of apparatuses). During the measurement the room was empty. The floor of the room was made of glazed plates. The walls and the ceiling were painted with pentaphtal paint which is a relatively slow gas absorber. There were very few pieces of furniture in the room and most of them were metallic. Smoking was prohibited in the laboratory and in neighbouring rooms.

The measurement was carried out with an air ion spectrometer UT-7509 [8,10] which was slightly rebuilt and supplemented with an *Iskra 226* computer. The program KAIS used for spectrometer control and data collection was compiled by H. Tannet. The program executed the measurement and recording of the mobility spectrum of small air ions of both polarities in 64 points located logarithmically uniformly by mobility.

The background spectra were measured in maximally clean room. After that some certain chemicals in very low concentrations were added to the air.

The concentrations presented in this paper were roughly estimated. Actual measurements of concentrations were not made. The concentrations were calculated by the estimated volume of the admixture evaporating from a surface of 1 cm<sup>2</sup> at  $T = 295$  K,  $p = 10^5$  Pa. The time of evaporation and the distance of the admixture dish from the spectrometer were taken into account in the calculations.

### Experimental results

The background spectra of one-second small air ions in laboratory air have a typical form (Fig. 1).

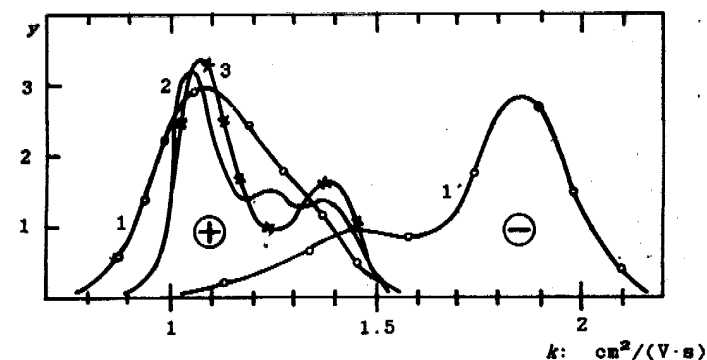


Fig. 1. Mobility spectra of small air ions. 1 and 1' - background spectra, monthly average (March 1986); 2 and 3 - traces of pyridines in the room (2 - the next day, 3 - a week after the experiments). The ordinate  $y$  of the spectra is in arbitrary units.

After the experiments with pyridine and its homologues and airing of the room, the mobility spectrum of positive air ions always contains three peaks, whereas 1.05 cm<sup>2</sup>/(V·s) is dominant. Pyridine, picoline, lutidines, and collidine influence the mobility spectrum of small positive air ions (Figs. 2-4). They do not influence the spectrum of negative air ions. On the wide background peak 0.7-1.6 cm<sup>2</sup>/(V·s) there are evident peaks 1.05 cm<sup>2</sup>/(V·s) (background after all pyridines), 1.2 cm<sup>2</sup>/(V·s) (2-picoline, 2,6-lutidine, collidine), and 1.4 cm<sup>2</sup>/(V·s) (2,3-lutidine, 2,4-lutidine). In the case of pyridine the peak is widened towards higher mobilities.

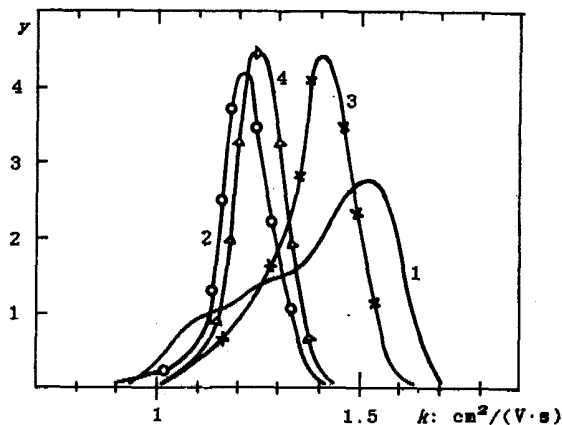


Fig. 2. The influence of pyridines on the spectrum of positive air ions. 1 - pyridine, 2 - 2-picoline, 3 - 2,3-lutidine, 4 - collidine.

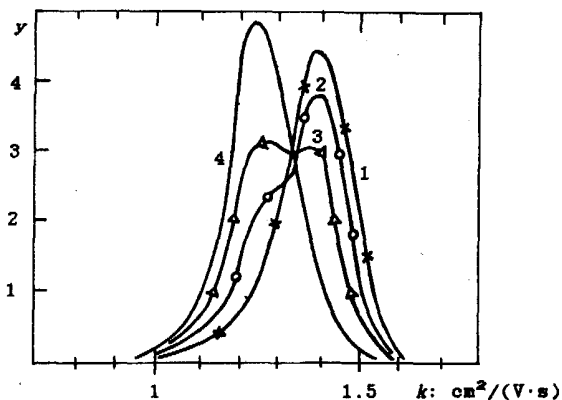


Fig. 3. The influence of dimethylpyridines on the spectrum of positive air ions. 1 - 2,3-lutidine, 2 - 2,4-lutidine, 3 - 2,5-lutidine, 4 - 2,6-lutidine ( $c \approx 10^{-2} \mu\text{g}/\text{m}^3$ ).

Fig. 3 presents the mobility spectra of various dimethylpyridines: 2,3-, 2,4-, 2,5-, and 2,6-lutidines. The mobility

spectra of 2,3-, and 2,6-lutidine have discrete peaks of  $1.4 \text{ cm}^2/(\text{V}\cdot\text{s})$  and  $1.2 \text{ cm}^2/(\text{V}\cdot\text{s})$  respectively. The mobility spectra of 2,4- and 2,5-lutidine are in an intermediate position, and have two peaks whose relations depend on the concentration of the admixture.

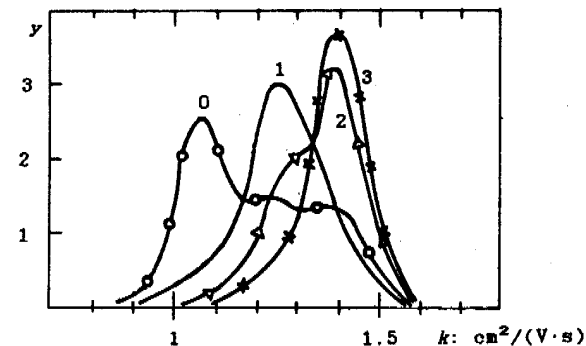


Fig. 4. The dependence of the spectrum of positive small air ions on the concentration of 2,4-lutidine ( $c_3 > c_2 > c_1 > c_0$ ,  $c_3 = 10^{-1} \mu\text{g}/\text{m}^3$ ,  $c_0 \approx 10^{-3} \mu\text{g}/\text{m}^3$ ).

#### Discussion

In recent studies of air ions in the troposphere using mass spectrometry and gas chromatography it is supposed that  $\text{NH}_4^+(\text{H}_2\text{O})_n$  are the final dominant positive air ions in natural air, however the composition of positive air ions is influenced by organic admixtures always present in the troposphere [5].

In addition to dominant air ions the atmosphere also contains  $\text{O}_2^+(\text{H}_2\text{O})_n$ ,  $\text{NO}^+(\text{H}_2\text{O})_n$ ,  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ ,  $\text{NH}_4^+(\text{NH}_3)_m(\text{H}_2\text{O})_n$ , etc., depending on temperature, pressure, humidity, age of ions, and the particular admixtures of the air.

The main parameters that determine the mobility of an ion in a gas are its mass and effective dimensions. The mass of an ion is determined by its chemical composition, the dimensions are determined by composition and other physical-chemical properties of the ion.

An increase in the concentration of an admixture or the appearance of new admixtures in the air leads to a change in

the composition of air ions on account of their collisions with the molecules of the admixture. As a result air ions with new chemical compositions are formed. Masses and dimensions, and consequently also mobilities of the ions are changed.

Our measurements show that in some cases admixtures with remarkably different molecular masses ( $\text{CH}_3\text{C}_5\text{H}_4\text{N}$ ,  $(\text{CH}_3)_2\text{C}_5\text{H}_3\text{N}$  and  $(\text{CH}_3)_3\text{C}_5\text{H}_2\text{N}$ ) give mobility peaks in one and the same region  $1.2 \text{ cm}^2/(\text{V}\cdot\text{s})$  (Figs. 2 and 3).

Pyridine, picoline, lutidines, and collidine have higher proton affinities than ammonium (Table 1) and they easily enter the reactions of proton transfer (Table 2) which take place at a reaction rate of about  $10^{-9} \text{ cm}^3\cdot\text{s}^{-1}$  [5].

Table 2  
Proton transfer reactions with pyridines

Initial compounds	Final products
$\text{C}_5\text{H}_5\text{N} + \text{NH}_4^+(\text{H}_2\text{O})_n$	$\text{C}_5\text{H}_5\text{NH}^+(\text{H}_2\text{O})_n + \text{NH}_3$
$\text{CH}_3\text{C}_5\text{H}_4\text{N} + \text{NH}_4^+(\text{H}_2\text{O})_n$	$\text{CH}_3\text{C}_5\text{H}_4\text{NH}^+(\text{H}_2\text{O})_n + \text{NH}_3$
$(\text{CH}_3)_2\text{C}_5\text{H}_3\text{N} + \text{NH}_4^+(\text{H}_2\text{O})_n$	$(\text{CH}_3)_2\text{C}_5\text{H}_3\text{NH}^+(\text{H}_2\text{O})_n + \text{NH}_3$
$(\text{CH}_3)_3\text{C}_5\text{H}_2\text{N} + \text{NH}_4^+(\text{H}_2\text{O})_n$	$(\text{CH}_3)_3\text{C}_5\text{H}_2\text{NH}^+(\text{H}_2\text{O})_n + \text{NH}_3$

Changes in the spectra may be connected with the above reactions, but other reactions are also possible (e.g. decay of complexes, changes of hydration rates, etc.). Measurements of mobility spectra of small air ions show that pyridine and its homologues manifest individual physical-chemical properties both in the reactions of proton transfer and in the reactions of cluster formation - decomposition.

#### Conclusions

1. Pyridines as nucleophilic chemical reagents have a strong influence on the mobility of positive small air ions of one-second age, whereas they do not influence the mobility of negative ions.

2. The form of the mobility spectrum of positive small air ions depends on the concentrations of the admixtures injected into the air, but on very low concentrations the effect is similar: a peak at the mobility  $1.05 \text{ cm}^2/(\text{V}\cdot\text{s})$  is induced.

3. Lutidines (dimethylpyridines) have a characteristic influence on the spectrum of positive small air ions. The mobility spectrometry of one-second small air ions makes it possible to identify 2,3-, 2,4-, 2,5-, and 2,6-lutidines at their low concentrations in air.

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