On the Appearance of Ninhydrinpositive Substances in the Atmosphere

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Abstract

This report is part of a larger work (entered at the Austrian Academy of Sciences on 20th June, 1959) which appears here without significant alteration and translated into English; it deals with the investigation of atmospheric organic nitrogen compounds. On some days in the course of these investigations the appearance of ninhydrinpositive substances could be established and at least some of them could be identified with great probability as amino acids. Observations are made about the appearance of these substances in relation to meteorological factors, and about the sizes in which particles of these substances may appear. Some remarks are added about their possible origin and the influence their appearance may have on life.

Introduction

Since the middle of the last century there have been a great many investigations into the presence of nitrogen compounds in the atmosphere and in precipitations. By far the largest number of these investigations have involved both ammonia and its salts and nitrates and nitrites, whilst only relatively few investigations about organic nitrogen compounds have been made. The different views on the formation and cycles of these substances (and the significance which individual authors attribute to the various sources of atmospheric nitrogen compounds) prove the complexity of this problem. Although a number of questions connected with the atmospheric inorganic nitrogen compounds remain unsolved, the uncertainty increases as soon as the appearance of organic nitrogen compounds is considered, especially since there are very few works which deal with the nature of these compounds. Indeed one dare say that this field of research is hardly explored, as until now almost the only goal of investigation has been the determination of the amount of albuminoid nitrogen, i.e. the ammonia released from organic matter in precipitation when treating it with oxidizing agents, or by Kjeldahl digestion. (These are both summary methods.) Thus it is not possible to decide whether this albuminoid nitrogen is produced by fragments of organic matter, bacteria, pollens etcetera, or from more simple nitrogen compounds, e.g. amino acids or amines. As far as is known, FONSELIUS (1954) was the first to find in precipitations the most simple nitrogen compounds of organic matter (i.e. amino acids) using the methods of chromatography, which are especially fitted for this kind of research.

Different explanations of the appearance of amino acids in the atmosphere are conceivable. They may be set free by the decomposition of organic matter or even perhaps arise in connection with the combustion of solid or liquid fossil fuels. Finally it is possible that higher organic nitrogen compounds arise from a synthesis from more simple compounds, similar perhaps to that of MILLER (1953, 1955, 1957) or from other synthesis hitherto unknown. All these possibilities may be taken into con-

sideration. As early as 1934 TREIBS (1934, 1935) produced evidence of relatively unchanged chlorophyll- and hæmin-derivatives in crude oils, coal and bituminous rocks. (In crude oils he found porphyrinderivatives in an amount of 2γ—10 mg per 50 g crude oil.) It is quite possible that during combustion small amounts of these derivatives or fragments of them, escape into the air. Since these compounds contain nitrogen in the form of the pyrrol ring, according to the preservation of this ring or its splitting, the formation of more or less simple nitrogen compounds is possible. Just as these hæmin- and chlorophyll-derivatives survived almost unchanged for millions of years, so did amino acids in fossils. Thus alanine, glutamic acid, glycine, leucine or isoleucine and proline have been identified beyond doubt and valine less certainly by ERDMAN, MARLETT and HANSON (1954). These are almost the same amino acids which ABELSON (1957) lists as the most stable; so alanine may survive in solution for billions of years at room temperature, 100 years at 120 degrees and a few hours at 250 degrees. To the more stable amino acids may be added also aminobutyric acid, glycine, isoleucine, leucine, proline and valine, whilst all others are less stable. Even if the existence of free amino acids in fossil fuels is not very probable, because in organic fuel of lesser age only such higher compounds as sugars, waxes, fats and resins have been found (cited after ABELSON, 1957), it is possible that aliphatic nitrogen compounds may be present from which under special conditions amino acids or similar compounds could be synthesized. In view of the preferred absorption of nitrogen compounds in water which is favoured by certain weather conditions, this synthesis could take place in little water droplets whereby the smallest particles of dust, aerosol or seasalt could act as catalysts for chemical or photochemical processes. Thus in the smallest space, i.e. in the droplets themselves, it is possible to conceive conditions which sometimes differ from those predominant in the atmosphere as a whole. So, for example, in contradiction to the surrounding oxidizing atmosphere, reducing conditions, at least for short periods, would be possible in these small spheres, producing reactions which could otherwise occur only with considerable activation energy and in very small yield in an oxidizing atmosphere. The oxidation of SO_2 to SO_3 could be cited as an example for the establishment of such conditions, since, owing to industry, home heating and traffic aerosol, a relatively large amount of these compounds is brought into the air. This or similar processes would, like a Miller synthesis, in which u.v. radiation provides the necessary energy, lead to the formation of amino acids. However, the great reactivity of many rather simple organic nitrogen compounds and their great affinity for water and carbon dioxide makes a large number of reactions possible.

The substances found, or the compounds from which they originate, could have been formed near the place where the sample is taken or carried from further afield by air or winds. Thus, e.g. ÅNGSTRÖM and HÖGBERG (1952), gave evidence that the content on NH_4N resp. NO_3N in precipitations depend on the air masses out of which they are formed (see table 1).

Table 1.

Number of invest. precipitations	air-mass	NH_4N	tropic air = 1	NO_3N	tropic air = 1
20	tropic	0,0354	1,00	0,0142	1,00
92	polar	0,0262	0,74	0,0131	0,92
5	arctic	0,0172	0,49	0,0094	0,66

Description of Apparatus and experimental Conditions

The air investigations were carried out in a laboratory at Strudlhofgasse 4, Vienna IX, within the centre of the city, close to streets with heavy traffic. Just below and immediately opposite the laboratory is situated a small petrol station. The air-samples were taken out of the atmosphere at an approximate height of 10 metres above the ground by a glass tube with a diameter of 10 mm. The outer end of the glass tube was bent downwards. To keep out dust and those nitrogen compounds which together with the dust enter into the atmosphere, the air was filtered with filters of different pore-size. The air was then passed into a bubble-tube, as already described in similar form by other authors (see fig. 1). A water-jet vacuum-pump sucked the air in; the rate of flow of the air was regulated

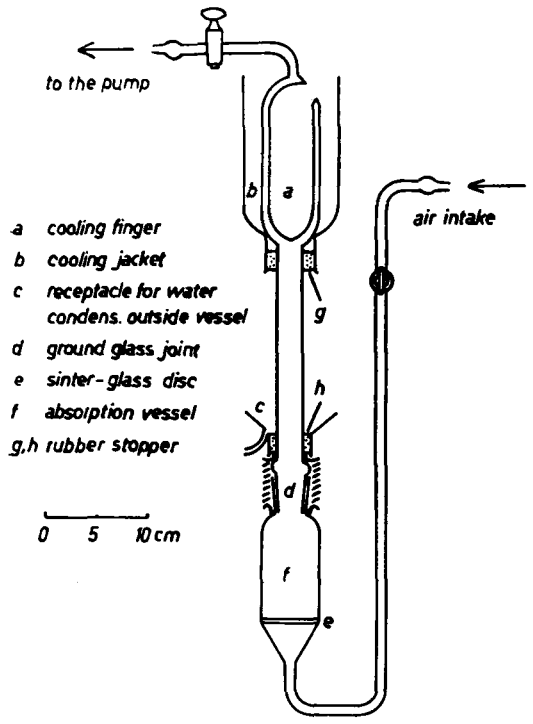

Fig. 1. Absorption-vessel.

by a set of capillaries and pressure variations were eliminated by a glass reservoir positioned in front of the water-jet pump. The air volume was determined by a rotameter used in connection with a manometer. The passing of the air between a cooling finger and a cooling jacket (both ice-cooled) ensured a sufficient cooling of the water-saturated air to make losses of absorption-fluid insignificant (even in experiments lasting some days and in outside temperatures of 25 degrees C and higher).

The flow-rate was about 120 litres an hour under normal pressure, which meant approximately 1 m^3 if the test lasted for 9 hours (as was usual). 150 cm^3 of twice-distilled water was used as absorption-fluid (for the second distillation a quartz distillation set was used) and to it was added 0.2 cm^3 glacial acetic acid per analysis. Acidification of the absorption-fluid with acetic acid instead of with hydrochloric acid proved more useful, as the fine bubbles formed while using the former remained longer without much coalescence on their way through the liquid; a good mixture of the air with the liquid was thereby assured.

Under reduced pressure (water pump) the absorption-fluid was evaporated to dryness at a temperature of 35° C. The residue was taken up with a drop of doubly-distilled water and investigated by circular paper chromatography. To filter the air, either Weissband filters of Schleicher and Schüll or membrane filters No. 5 of Sartorius, Göttingen, were used. The exact pore-size of the "Weissband" filter is unknown to the author, but according to RÖMPP (1958) it may be about 5 μ. The manufacturer of the membrane filter used gives its pore-size as 0.25—0.40 μ. The air was filtered prior to its examination to prevent greater contamination of the sample. Later, when two devices both with these filters were running simultaneously, the different pore-size of the filters made possible a separation of the investigated particles according to size and so gave evidence about the approximate particle-size of the different fractions.

Owing to its good discriminating power and long running-time which permitted an easier control of the running chromatogram, filter paper 2045 b made by Schleicher and Schüll was used. The substances were arranged in a circle with a radius of 2.0 cm around the centre of the chromatogram in 6—8 equal distances. This arrangement and the applying of test substances besides the substances under investigation made it possible to compare R_f-values and colours, and corresponds to the method described by GIRI and RAO (1952). A butanol/acetic acid/water-mixture was generally used as solvent for the chromatography, also several times water-saturated phenol. For the few two-dimensional chromatograms which were carried out, the above-mentioned combinations of solution mediums were used. In general the chromatograms were developed by a 0.2 % ninhydrin solution in butanol and acetic acid and then heated. The development aiming at finding ninhydrinpositive substances in the atmosphere was used because, in the adopted arrangement of tests, the test for reducing substances (with ammoniacal silver nitrate solution, benzidine and with triphenyltetrazolium chloride) as well as for phenols (with $FeCl_3$) remained negative. Repeated blank tests as well as investigations of the air with a negative ninhydrin reaction on the chromatogram, which can be counted as negative blank tests, showed the freedom of the

chemicals used from ninhydrinpositive substances.

From the local meteorological conditions, temperature, air pressure, relative humidity, wind and cloudiness were recorded, though summarily. At the end of the experiments, the filter contamination was estimated visually. To these data were added those of the Central Institution of Meteorology and Geodynamics in Vienna, concerning air masses and duration of sunshine at the time of experiment.

Results of Investigations

Duration and Classification of Experiments

On average, tests were run for 9 hours, mostly between 9.00 a.m. and 6.00 p.m. Longer investigations were carried out from January 28th to March 1st, 1958, covering a period of 33 days, another from March 24th to March 29th, followed by one from March 31st to April 4th, 1958, and finally one running from April 17th to April 26th, 1958. A day-and-night series was run uninterrupted from 3rd to 13th July, 1958 and carried through with 3 devices so that 46 air samples were collected and tested. All in all the atmospheric air was tested for ninhydrinpositive substances on more than 100 days, and the results of these investigations were correlated with general meteorological conditions, prevailing air masses and local weather conditions.

The experiments can be divided into two groups. Firstly when two similar devices were available, an attempt was made to find out the approximate order of magnitude of the investigated substances by inserting filters of different pore-size in front of the absorption vessel. Later on, when the interest was directed more to the identification of the substances, one apparatus was used to provide the material for the daily air examinations, whilst in the second apparatus material was collected (during a longer period) for chromatographic investigations of substances absorbed out of the air. These longer tests were always run for several days and during this period the same acetic acid solution remained in the absorption vessel. In the first investigations the same filter as used in the other apparatus was kept in the filter holder for the whole test. Later on it was replaced daily by a new filter to eliminate changes which might have been caused by filter contamination. Thus analogous working conditions were obtained on both devices. On the whole, the long running test did not show any other quantitative and qualitative result as would correspond to the sum of the individual test-results obtained within the same period.

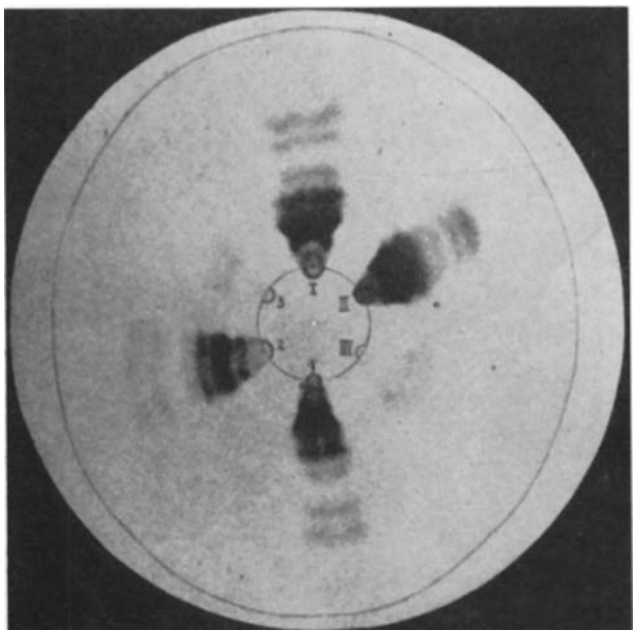

Fig. 2. Chromatogram of substances obtained beyond Weissband- and membrane filter.

I, II, III — Samples taken beyond the Weissband filter on October 14th, 15th and 18th, 1957.

1, 2, 3 — Samples taken beyond the membrane filter No. 5, taken on the same days.

III and 3 — almost negative results (obtained beyond both filters) of samples taken on 18th October, 1957.

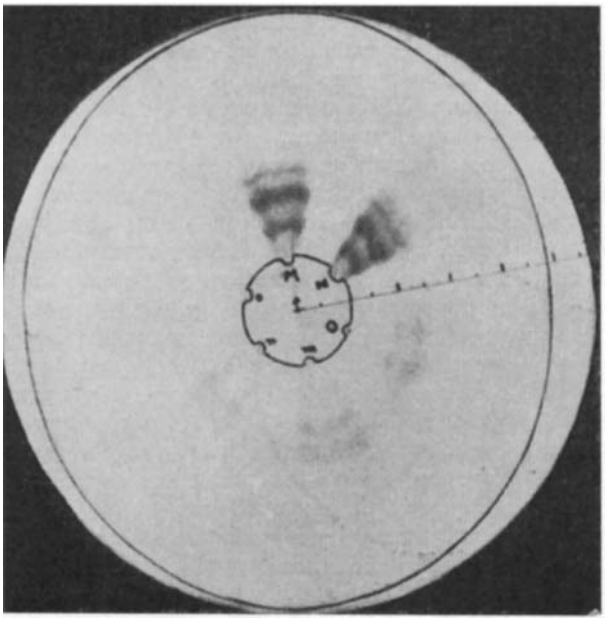

Fig. 3.

Result of using Filters with different Pore-Size

Unfortunately there exist only a few results giving information about the size of particles which cause ninhydrinpositive reactions or which occlude ninhydrinpositive substances. So, for instance, the chromatogram of the 14th and 15th October, 1957 (fig. 2 black and white photograph from a colour slide) shows that on both days the chromatographically discovered substances were present in the air in such size that they passed through the Weissband filter (pore-size approximately 5.0 μ) as well as the membrane filter (pore-size 0.25—0.40 μ) in almost the same amount and compo-

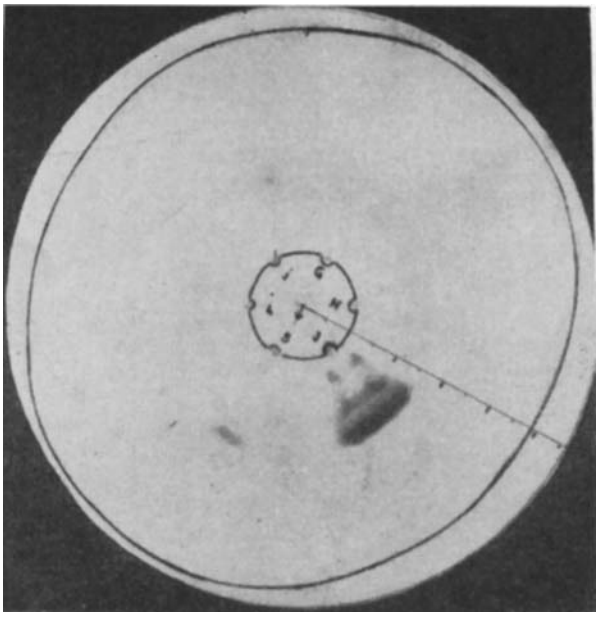

Fig. 3. Fig. 4. Chromatograms of substances obtained beyond Weissband- and membrane filter.

Capital letters — Samples taken beyond Weissband filter.

Small letters — Samples taken beyond membrane filter No. 5.

J (j) — indicates tests from 29th October, 1957.

M (m) and N (n) — those from 6th and 7th November, 1957, respectively.

The other letters denote days on which beyond the Weissband filter as well as beyond the membrane filter negative or almost negative results were obtained.

sition. Chromatographically there can be found only little difference of substance composition between samples collected beyond the Weissband filter and these found beyond the membrane filter.

Different results were obtained from similar investigations carried out on 29th October and 6th and 7th November, 1957. Beyond the Weissband filter a decrease in the number and intensity of the spots was observed and there was a more or less complete absence of positive results beyond the membrane filter (fig. 3 and fig. 4).

Using the same experimental arrangement for several tests, results similar to the last were obtained.

As a result of these investigations it seems to be evident that with the decrease in the number and intensity of the spots, either the particles increase in size or else they are occluded to larger particles.

It was unfortunate that on days with many ninhydrinpositive substances in the air, investigations with only one kind of filter were carried out, so that it was not possible to confirm the results of the 14th and 15th October, 1957.

From air pollutions according to KATZ (1956) only the smoke of oil, tobacco and carbon and NH_4Cl fumes could pass both filters. In addition to this, the Weissband filter allows SO_3 mist and some of the smaller bacteria, to pass through.

Results of chemical Investigations

During extensive preliminary trials positive results were obtained only by the before-mentioned method when using ninhydrin as developer. This result by no means proves the absence of other substances in the atmosphere but is due to the limitations inherent in the method used. Among the ninhydrinpositive substances chiefly amino acids, amines and perhaps aminoaldehydes have to be considered. By evaporation to dryness at 35° C, no compounds volatile at this temperature, i.e. the greater part of the gaseous or liquid simple aliphatic amines, are included in this investigation. Substances insoluble in water were likewise excluded. However, salts of these compounds often show a different reaction with regard to solubility in water and volatility. A partial salt formation could take place either in the air or later during the absorption in the bubble tube. Assuming

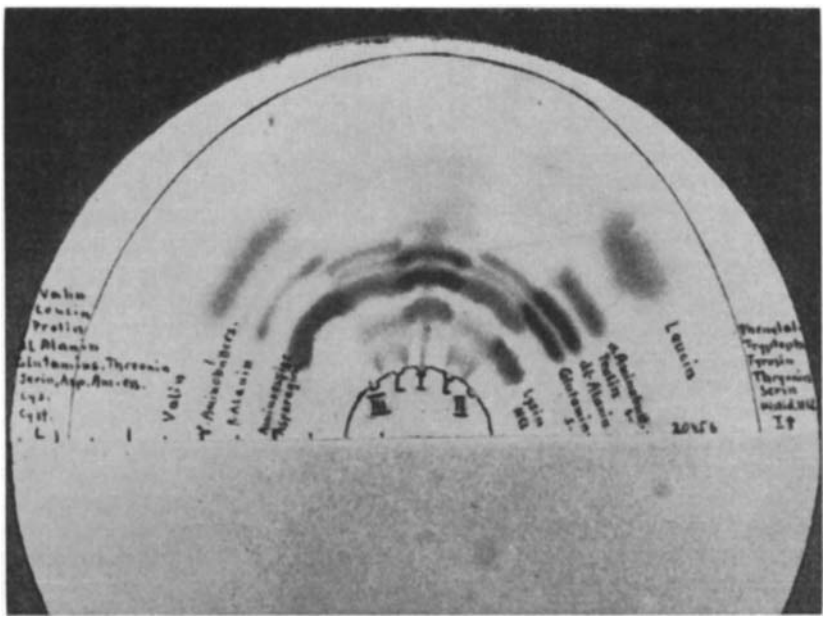

Fig. 5. Test substances and substances obtained from the air, chromatographically compared.
L — means the mixture of substances from the air.
I, II, III—the test substances used on the chromatogram.

that the last-mentioned reaction is of no great importance, at least a certain number of the substances found can be considered as amino acids, for the following reasons:

1. The substances obtained from the air behaved similarly to the amino acids used as test substances, both in chromatograms with a butanol/acetic acid/water-mixture as solvent (see fig. 5), and in those where the sample was divided and one part chromatographed with the above solvent, the other with water-saturated phenol.

2. The ninhydrinpositive substances did not show up if the chromatogram was treated with copper carbonate before its treatment with ninhydrin. According to CRUMPLER and DENT (1949), this is charateristic of α-amino acids, as other ninhydrinpositive substances remain ninhydrinpositive after such treatment.

3. A spot which appeared yellowish after ninhydrin treatment, and which behaved similarly to proline used as a test substance, appeared after isatine-spraying as a faint blue. (A similar blue was shown by some of the other substances in question, and the same reaction is known for some amino acids.)

4. The only investigation of precipitation (snow) which was made showed ninhydrinpositive substances in such quantity that they remained unseparated on the chromatogram. As this sample was not subjected to any other treatment besides filtering and boiling down, formation of these substances, while being collected in the absorption-vessel, does not seem to take place. FONSELIUS' (1954) findings on amino acids in precipitation would support this view.

In cases where distinct positive results were obtained on the chromatogram, the concentrated absorption-fluid showed a yellowish tinge, a fact which agrees with the information the author received from Fonselius, who also got a yellowish residue from the distilled sample when investigating precipitations. Yellow-coloured substances had been observed as early as 1853 by BARRAL (1853) in rainwater and BOUSSINGAULT (1858) in fog. Both authors considered them as organic substances and found that they released ammonia on treatment with alkali. At MILLER's (1953, 1955, 1957) successful experiments to produce amino acids under possible primitive earth conditions yellow polymers were formed too showing a very intense ultraviolet absorption.

From the chromatographic results, those substances isolated from the atmosphere seem almost certainly to be glycine, alanine, valine and leucine and (less certainly) glutamic acid, aspartic acid and proline.

The absence of ammonium acetate, which as a hygroscopic substance should have appeared, was remarkable. Only during longer experiments were hygroscopic substances found, particularly when only one filter was used for the whole experiment. It is possible that such small quantities of ammonia can be absorbed on the filter, or that it combines with sulphuric acid on the filter or in the absorption-fluid, thereby forming ammonium sulphate which is hardly hygroscopic.

Relation to meteorological Factors

On approximately 25 days out of more than 100 investigated days positive results were obtained. Among them were one third faintly positive. Though the strongly positive results were to some extent dependent on the prevailing air masses, the number of these results is too small (16) to establish a real relation. Considering all different tropical air masses together, positive results for tropical air masses were obtained 9 times, for mixed air masses 2 times, and for arctic 5 times. As tropical air masses prevailed during the testing period the results loose some of their significance. On the other hand, lightly foggy or hazy weather with high air-humidity and little altered or falling air pressure was, almost without exception, a precondition for positive results. On days with heavy fog the presence of these substances could not be proved, either because this kind of weather does not assist their formation or because they are absorbed by droplets too large to pass the filter. In this connection the only investigation of precipitation (snow), carried out on February 27th, 1958, may be mentioned. In that instance so great was the amount of ninhydrinpositive substances present that they remained chromatographically unseparated, whilst the air investigation of the same day showed a wholly negative result. Air investigations on the two preceding days, i.e. February 25th and 26th, 1958, days without precipitation, showed the presence of a large number of ninhydrinpositive substances. Of

course it is not possible to decide from this single test whether these substances are absorbed to a high degree by snow flakes (or rain drops). The much higher frequency of positive results obtained during the cold seasons with rather stagnant air masses and little turbulence may indicate a possible connection between the appearance of these substances and the combustion of solid and liquid fossil fuels. Nevertheless, more or less positive results were also found during the warm season, though only in small number. There existed no distinct correlation between the visible filter contamination and the occurrence of positive results. The substances found could also be derivatives of compounds diffused from the sewers and the nearby Danube Canal into the atmosphere, where they accumulate. In such places decomposition of organic matter may take place on a large scale, and under favourable atmospheric conditions these decomposition products may escape in relatively large quantities into the air. Suitable meteorological conditions would be falling or at least constant air pressure and a larger temperature gradient from the warmer sewers to the colder open air. Inversion layers and little air motion would favour an accumulation of these substances in the atmosphere, where they can be subjected to different chemical alterations. In this context it may be mentioned that according to CAUER (1956) a higher decomposition rate of organic substances and greater biological activity, whereby the so-called "ammoniacal substances" are formed, produce a rise in the pH-values of the atmospheric condensation water.

That the turbulence is of some importance could be concluded from the investigations run day and night in July, 1958, where the results obtained during the least turbulence (viz. in the early morning and evening) though poor, turned out to be better than those produced in investigations carried out at midday, the time of the highest turbulence, when there were almost no results at all. The vapour layer, which varies in thickness, according to the season, must also be considered. Since, according to LÖHLE cited after Band, 1957, the upper limit of the vapour layer lies during the cold season at approximate heights of 400—500 m, the thickness of this layer can increase by convection during summer to 3,000 metres and more. The differences of results between summer and winter may thus be at least partially explained, for during summer the substances looked for might be diluted to such an extent that they escape detection.

It could also be that some of the substances in question were assimilated by green plants during the vegetation period.

In general, negative or only faintly positive results proved to be independent of meteorological factors.

Error analysis

Among the various possible errors there are only a few relevant enough to alter the results significantly. Summarizing them, two main sources have to be distinguished:

1. errors which occur in taking and treating the sample,
2. those which may be due to chromatography.

With reference to 1.

a. Fluctuation of the air-intake volume is of no importance as qualitative results were the principal aim. The filter contamination after sucking 1 m^3 of air does not lower the flow-rate significantly. Only the air humidity seems to influence the flow-rate by altering the pore-size of the filters. This rather unimportant effect was compensated by adjusting the appropriate capillary in the capillary set. From the readings of the rotameter and manometer a flow-rate accuracy of $\pm$ 10% was established.

b. Two faults caused by the filtering could falsify the results qualitatively and quantitatively in a way difficult to correct and to estimate. The first, described by JUNGE (1956), is the considerable absorption of some gaseous air constituents by millipore filters. THOULET (1903), noted an extraordinary ammonia absorption on paper filters. Secondly, there is the possibility that substances absorbed on the filter react and that the reaction products diffusing after saturation through the filter show compounds which do not exist in the open air.

c. Owing to the cooling at the end of the apparatus and the low air flow-rate, losses of absorption-fluid by spraying and evaporation are, as measurements showed, insignificant.

d. Substances remaining in the frit after removal of the absorption-liquid have no influence on the investigations which follow; this is proved by the absence of any reaction after high positive results. Whether a loss of material in the process of the thorough cleaning of the absorption-vessel takes place would have to be investigated separately.

e. Losses during the evaporation depend on the vapour pressure of the substances under examination. As the evaporation of volatile substances was the purpose of the method used, this effect need not be considered as an error.

f. For the insolubility in water, par. e. applies, as only substances soluble in water were the aim of the investigation.

g. Any losses resulting from the application of the substances on the filter paper for chromatography need not be considered.

h. Finally, the argument that the acetic acid used may serve as culture medium for spores and bacteria passing the filter, must be taken into consideration. Owing to the low temperature, which is unfavourable to the growth of microorganisms, and the relatively short time between absorption and evaporation, the formation of these compounds seems very improbable, although not quite impossible. Such effects should certainly occur more frequently during the warm seasons, but in fact positive results from the air investigations were much more often obtained during the cold period. Finally, the finding of amino acids in precipitation by FONSELIUS (1954) and of ninhydrinpositive substances by the author in snow do not support the view of a genesis of these substances through bacterial activity in the absorption-fluid.

re. 2.

a. Not only the R_f-values themselves but also their relation to each other can be altered as well by the contamination of the substances examined with other compounds in the atmosphere, as by inconstant temperature during the chromatography. Also the colours of the developed chromatograms may to some extent be influenced by contamination. The variation of these possible hindrances to the chromatography is responsible for the impossibility of reproducing the chromatograms exactly. Hindering substances could be removed, for example, by ion exchange.

b. Especially in these chromatograms where heating is necessary for the removal of solvent, e.g. such as run with phenol, losses occur according to BRUSH, BONTWELL, BARTON and HEIDELBERGER (1951). Thus substances which are only present in low concentration may disappear in some chromatograms and so make it difficult to compare them with those where heating is not necessary.

Summary and Discussions of Results

On some days in the course of investigating the atmospheric air over a period of more than a year, ninhydrinpositive substances were found, which can fairly safely be considered as amino acids. Glycine, alanine, valine and leucine have been identifired almost to acertainty, glutamic acid, aspartic acid and proline less surely. Some of the substances may be amines. These substances appeared much more often and in greater quantity during the cold season. The amount of the individual compounds reached a maximum of a few γ per m^3. A more abundant appearance of the substances was paralleled by a yellowish tinge of the concentrated absorption-fluid.

A direct connection with the atmospheric conditions and air masses could not be confirmed beyond doubt, but local meteorological factors like high humidity with haze, reduced visibility and falling or almost stable air pressure, indeed seem to be suitable conditions for the formation or preservation of these substances. The greater frequency of their appearance during the cold season can hardly be related to the combustion of liquid and solid fossil fuels alone. Meteorological factors prevailing at this season may be involved in the formation, preservation or decay of these compounds. Such meteorological factors could also stipulate conditions which enable nitrogen compounds, formed in connection with decomposition of organic matter in sewers and rivers to escape in greater amounts into the air and to accumulate there. To find a possible connection between the appearance of the above-mentioned substances and the different air masses, further investigations would have to be carried out simultaneously in several places. Independent of any hypothesis about the genesis and source of the substances found,

the changes they have to undergo by chemical or photochemical influences, must also be considered. Thus the genesis and preservation of the substances could be due to the simultaneous influence of certain local factors and of those which are effective over extended areas.

It is possible that in some methods of NH_3 determination a part of these substances is included.

Many nitrogen compounds have a direct effect on human organism and it seems possible, therefore that the amount of these compounds found on certain days in the atmosphere, may be sufficient to alter the pH-values of skin or mucous membranes (CAUER, 1956) or to cause troubles of an allergic nature in persons so disposed. But also these nitrogen compounds could become effective indirectly, through microorganisms whose growth, metabolism and augmentation they can further or hinder, characteristics which allow the determination of such substances by biological methods, i.e. with the aid of microorganisms. Thus the old miasma theory, however restricted or altered might possibly have some justification after all.

There may be a connection between these compounds and vegetation. The decrease of the substances could, during the vegetation period, be related to their assimilation by plants, the uptake of nitrogen compounds in small amounts by plant elements above ground being well known. Alternatively, WARBURG (1957) referred to the importance of two systems, alanine-aspartic acid and glutamic acid in connection with the carbon dioxide transfer at the photosynthesis of green plants. It would be of interest to know definitely whether a direct supply of those or other amino acids in the air would influence the assimilation by plants.

In view of limited means and the difficulties inherent in all kinds of investigations depending on meteorological factors, the results obtained cannot be considered as final. Therefore it may be of some interest to continue the investigations and to advance the position so far reached. By these and other investigations it seems already that known amino acids or substances closely related to them are, though in extremely small amounts, widely spread in nature outside of organic matter.

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