Gas chromatographic determinations of atmospheric He, Ne and H₂

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Atmospheric He, Ne and H₂ have been determined simultaneously by gas chromatography without any pre-purification procedures for enrichment. Repeated analyses of atmospheric air samples collected in Matsuyama, Japan from 1982 through 1984 have given the following average values with respective standard deviations; 5.20 ± 0.02 ppm for He, 18.4 ± 0.1 ppm for Ne and 0.83 ± 0.02 ppm for H₂. The obtained average values for the atmospheric He and Ne are in good agreement with the commonly accepted values. The concentration of H₂, however, is considerably fluctuating even in a short duration less than half an hour, and is affected by meteorological conditions. In particular, the H₂ concentration negatively correlates with wind velocity. This trend is clearly seen in rainy days.

Exhaust gases from automobile engines are highly enriched in H₂, on the order of a percent by volume. The H₂-rich exhaust gases are being diluted by less polluted air, and the rate of dilution seems to depend strongly on the wind velocity and precipitation. The average value of H₂ concentrations measured in Matsuyama is definitely higher than the background value in surface air of Northern Hemisphere of 0.584 ppm, but comparable to that in the polluted air in Mainz, West Germany reported ten years ago.

INTRODUCTION

The composition of atmospheric air of the Earth is related to various geochemical problems such as evolution of the atmosphere and ocean of the Earth, environmental pollutions by human activities and so on. The atmospheric air at ground level, on the other hand, is important for practical works involving chemical analyses of N₂, O₂ and rare gases in various gas samples of geochemical interest, since their concentrations in the atmospheric air are accurately known and constant enough to be used as the standards. Craig *et al.* (1967), for example, analyzed dissolved N₂, O₂ and Ar in sea waters by gas chromatography, their calibration of which was made with atmospheric air. In the rare gas studies by the mass spectrometric method (Bieri *et al.*, 1966; Podosek *et al.*, 1980; Smith and Kennedy, 1983), atmospheric

air with the constant elemental and isotopic abundances of He, Ne, Ar, Kr and Xe has been used as the indispensable standard for the calibration procedures.

For the seismo-geochemical purpose, routine analyses of subsurface gas samples have been made in our laboratory by gas chromatography (Kawabe, 1984/85), in which atmospheric air is used as a very convenient composite standard gas for He, Ar and N₂. Helium in atmospheric air, however, has been rarely used as a standard in gas chromatographic analyses, because the chromatographic separation between He, Ne and H₂ in atmospheric air is usually difficult, and because the concentration of He in air is fairly low, 5.24 ppm (Glueckauf, 1951). Considerable efforts have been made to remove such difficulties and to apply the gas chromatographic method to seismo-geochemical studies (Kawabe *et al.*, 1981; Sugisaki *et al.*, 1982; Kawabe,

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1984/85), through which a chromatographic technique for the effective separation of the atmospheric He, Ne and H₂ under room temperature conditions has been developed in our laboratory.

Itself is developed with the intention of utilizing atmospheric air as a composite standard gas for He, N₂ and Ar analyses of our routine works, it is also applicable to the simultaneous determinations of atmospheric He, Ne and H₂ concentrations themselves without any pre-purification procedures for enrichment. At the early stage of our seismo-geochemical work, we found that the concentration of H₂ in atmospheric air is considerably variable, and that the variation is probably related to weather conditions. The H₂ concentration, therefore, has been measured in the course of our routine works for the last three years in order to reveal the average H₂ concentration in the air of our area and the magnitude of the variation. The atmospheric He and Ne concentrations themselves have also been determined repeatedly for the last three years for the following reasons; (1) The absolute accuracy of our routine He analyses and the long-term credibility can be evaluated. (2) The concentrations of He and Ne in the atmosphere are widely accepted to be 5.24 and 18.18 ppm, respectively. These values, however, are based on the original works conducted about 40 years ago (Glueckauf, 1951). The other values published since then are extremely limited. (3) Our simplified gas chromatographic method is less precise in an individual analysis than the other sophisticated methods like the mass spectrometric isotope dilution method. But this drawback of the present method is overcome to some extent by repeating independent analyses many times so as to reduce the resultant statistical errors for the most probable estimates.

In this paper, the results of our gas chromatographic determinations of atmospheric He, Ne and H₂ concentrations are presented.

EXPERIMENTAL

The gas chromatographic method used in this study is almost the same as that described elsewhere (Kawabe, 1984/85). An Ohkura 802 TD gas chromatograph equipped with an Ohkura AM 101 DC microvoltmeter as an amplifier was used. The detector of a tungsten-filament katharometer was operated with a filament current of 120 mA. The carrier gas was oxygen at a flow rate of 23 ml/min. The separation between He, Ne and H₂ in atmospheric air was made at room temperature by using the following combination of the two absorbent columns: A 5 m column packed with 60/80 mesh Unibeads C (molecular sieving carbon), connected with another 3 m column packed with 60/80 mesh Molecular Sieve 5A. The columns were stainless or copper tubing of 4 mm O.D. and 3 mm I.D. These columns were activated at temperatures between 230 and 250°C for about 7 h.

Unibeads C is more effective for the separation of He, Ne and H₂ but less effective for the separation of N₂ and Ar than Molecular Sieve 5A. On the other hand, CO₂ can be absorbed irreversibly by Molecular Sieve 5A, but CO₂ elutes from the column packing of Unibeads C very slowly at room temperature. This slow elution of CO₂ is a disadvantage due to the long analysis time for atmospheric air samples. Therefore, the chromatographic properties for the effective separation of the atmospheric He, Ne and H₂ at room temperatures with a reasonably short analysis time, cannot be obtained by the single use of each absorbent column. But such properties are readily overcome by the use of the column combination of the two absorbents, because the inconvenient chromatographic properties of each absorbent can be replaced or reinforced by the favorable properties of the other as a net effect.

Samples of atmospheric air were collected outside the building of Department of Earth Sciences, Ehime University, which is located in the northeastern part of the city of Matsuyama. The air samples were taken either in Tedlar Bags

(gas sampling bags made of polyvinyl fluoride film) of 10l through a silica gel column with a manual pump or directly in 2.5ml gastight-syringes. After thermal equilibration in the laboratory, 2ml each of them was injected into the gas chromatograph with the syringe. When the Tedlar Bag was used for sampling, replicate measurements were made for aliquots of the air sampled in the bag. When it was not used, the direct sampling with the syringe and the subsequent measurement were repeated.

Elution peaks of respective components were recorded on a pen recorder, and the peak areas were calculated from heights and half-widths of the respective peaks. The peak areas thus obtained were found to be linear against the injected volumes of each component up to

100 μ l from the level of air samples; No significant systematic departure from the linearity could be found in the relationships between the peak areas and injected volumes of the pure gases, and between the peak areas and a gas mixture of the atmospheric air with and without small amounts of He, Ne and H₂. For the calibration of He, Ne and H₂, therefore, different volumes of their pure gases (25 - 75 μ l) were injected repeatedly with a gastight-microsyringe in each run. All the syringes used were recalibrated by us.

An example of the gas chromatogram of atmospheric air is shown in Fig. 1. The chromatogram of the gas with 0.83% He, 3.1% Ne, and 0.36% H₂ is also shown in Fig. 2. H₂ is completely separated from the pair of He and

Fig. 1. An example of the gas chromatogram of atmospheric air. Amplification factors relative to that for Ar are shown. The chart speed is 20mm/min for the portion of He, Ne and H₂ and 10mm/min for Ar and N₂. The column temperature is 27°C, and the other experimental parameters are given in the text.

Fig. 2. The chromatogram of a gas with 0.83% He, 3.1% Ne and 0.36% H_2 . The injected volume was 0.1 ml. The amplification factor is 1/32 of that for the He-Ne- H_2 portion shown in Fig. 1, and the other experimental conditions are the same as those for the example shown in Fig. 1.

Ne, and the He peak is almost completely separated from the Ne peak. The elution of He, Ne, H_2 , Ar and N_2 in air samples is finished in this order within 25 min.

RESULTS AND DISCUSSION

Results

Table 1 lists the results of simultaneous determinations of atmospheric He, Ne and H_2 . These values are expressed in ppm of the dry air volume. The results for air samples collected directly in gastight-syringes were corrected to the dry air values with the humidity, air temperature and barometric data by the JMA Matsuyama Observatory. The corrections were mostly less than 2%. Figure 3 shows the frequency distribution of the atmospheric H_2 concentrations in Matsuyama from May 1982 to September 1984. The H_2 data are given as averages of the replicate measurements on the

same day. Most of these data have been obtained in our routine runs, in which atmospheric He and Ne were not determined. In Table 2, the average for all the H_2 data shown in Fig. 3 and the magnitude of the variation is summarized and compared with the global background values and the local value from Mainz reported by Schmidt (1974 and 1978).

The weighted means for all the daily means of He and Ne determinations are calculated along with the standard deviations of the weighted means (Table 1). However, an equally weighted mean, instead of the weighted mean, is given for the atmospheric H_2 determinations from the following reason; The H_2 concentration is found to change as shown below, and the analyses of H_2 in the air samples collected at different times can not be dealt with as in the case of He and Ne determinations. Therefore, an equally weighted average and the standard deviation are calculated for the atmospheric H_2 concentration (Table 1 and 2).

Helium and Neon

The present results are compared with the literature values in Table 3. The currently accepted values of atmospheric He and Ne are 5.24 ± 0.004 and 18.18 ± 0.04 ppm, respectively. These values have been compiled by Glueckauf (1951) based mainly on his original work (Glückauf, 1946). Recently, Oliver *et al.* (1984) have reported by isotope dilution mass

Fig. 3. Frequency distribution of the analyses of atmospheric H_2 concentrations in Matsuyama. The H_2 data are given as the averages for measurements made on the same days from May 1982 to September 1984. Results listed in Table 1 are also included, except for those obtained after this period.

Table 1. Results of simultaneous determinations of atmospheric He, Ne and H₂⁽¹⁾

Date	He (ppm)	Ne (ppm)	H ₂ (ppm)
8/30/82	5.82 ± 0.31 (3)	—	0.86 ± 0.12 (3)
10/28/82	5.30 ± 0.13 (3)	—	1.22 ± 0.22 (3)
11/ 2/82	5.42 ± 0.11 (5)	—	—
3/16/83	5.16 ± 0.11 (14)	19.2 ± 0.3 (14)	0.93 ± 0.01 (14)
6/ 1/83	5.12 ± 0.05 (4)	—	0.81 ± 0.12 (4)
6/ 2/83	5.34 ± 0.07 (5)	—	0.82 ± 0.03 (5)
6/ 3/83	5.12 ± 0.24 (5)	—	0.94 ± 0.06 (5)
6/ 4/83	5.40 ± 0.22 (4)	—	0.78 ± 0.04 (4)
6/ 6/83	5.30 ± 0.14 (6)	—	0.70 ± 0.05 (6)
6/ 7/83	5.34 ± 0.15 (6)	—	0.65 ± 0.06 (6)
6/ 8/83	5.03 ± 0.07 (6)	—	0.60 ± 0.09 (6)
10/10/83	5.06 ± 0.11 (15)	18.0 ± 0.3 (15)	0.76 ± 0.03 (15)
12/29/83	4.68 ± 0.15 (5)	17.6 ± 0.4 (5)	0.77 ± 0.12 (5)
1/ 7/84	5.20 ± 0.11 (6)	18.6 ± 0.6 (6)	0.64 ± 0.03 (6)
1/19/84	5.20 ± 0.11 (3)	18.3 ± 0.5 (3)	1.05 ± 0.07 (3)
1/20/84	5.15 ± 0.14 (5)	18.7 ± 0.2 (5)	1.13 ± 0.19 (5)
1/27/84	5.27 ± 0.27 (6)	19.8 ± 0.9 (6)	0.77 ± 0.06 (6)
2/ 2/84	5.58 ± 0.14 (6)	19.8 ± 0.5 (6)	1.57 ± 0.35 (6)
2/ 8/84	5.49 ± 0.13 (6)	19.7 ± 0.6 (7)	0.99 ± 0.15 (7)
11/15/84	5.31 ± 0.06 (6)	19.4 ± 0.3 (6)	1.22 ± 0.11 (5)
11/27/84*	5.03 ± 0.09 (8)	17.7 ± 0.2 (8)	0.80 ± 0.03 (8)
12/ 1/84*	5.09 ± 0.06 (8)	18.7 ± 0.4 (8)	1.63 ± 0.04 (8)
12/ 8/84*	5.20 ± 0.10 (8)	18.3 ± 0.5 (8)	1.15 ± 0.03 (8)
12/15/84*	5.25 ± 0.08 (9)	18.1 ± 0.2 (9)	0.71 ± 0.06 (9)
Mean**	5.20 ± 0.02	18.4 ± 0.1	0.93 ± 0.06

(1) The mean in each run and one sigma error of the mean are listed. They are expressed in ppm of dry air volume. The figure in parentheses represents the number of measurements in each run. The quoted error includes the calibration error in each run;

$$s_i = ((\sum (x_{i,j} - x_i)^2)/(n_i(n_i - 1)) + s_{i,c}^2)^{1/2},$$

where $s_{i,c}$ denotes one sigma error for the mean value of the calibration factor in the run.

* The air sample was collected in the Tedlar Bag of 10l through a silicagel column, and aliquot volumes of it were used for the replicate measurements in the run. In the runs without this asterisk, air samples were directly taken in a syringe, and then injected into the gas chromatograph. Therefore, s_i 's for H₂ data in these runs do not represent the analytical error alone, because the H₂ concentration is considerably varying even in a short period of time.

** The weighted mean for the results of all the runs and one sigma error of the weighted mean are given for He or Ne; $\bar{X} \pm s = \sum (x_i/s_i^2)/\sum (1/s_i^2) \pm (1/(\sum (1/s_i^2)))^{1/2}$, where x_i and s_i are the mean and one sigma error of the mean in the i -th run, respectively. For H₂, however, an equally weighted average is given together with the standard deviation for the average (see text).

spectrometry that the He concentration in the near-surface air is 5.222 ± 0.017 ppm. The present result for the atmospheric He concentration by gas chromatography is in excellent agreement with the accepted value by Glueckauf or with the recent mass spectrometric value. The accuracy of the present method for He analyses is therefore concluded to be less than 1%.

The accepted value of atmospheric Ne, 18.18 ± 0.04 ppm, is actually the weighted mean of 18.21 ± 0.04 ppm from three analyses by

Glückauf (1946) and 18.1 ± 0.08 ppm by Chackett *et al.* (1949). The present value of 18.4 ± 0.1 ppm is in reasonably good agreement with the currently accepted value, suggesting that the accuracy of Ne analyses by the present method is not greater than 1.2%. The difference, however, is slightly larger than in the case of the He analysis. It is noteworthy that the error value given by Glückauf (1946) to his Ne result is too small, because his error value was estimated simply from the variance of his three measurements alone without incorporating cali-

Table 2. Average H_2 concentration in the surface air of Matsuyama, compared with those of other areas*

Location and period	H_2 (ppm)	No. of data**	Reference
(1) Matsuyama, Japan May 1982 - Sept. 1984	0.83 ± 0.02 (± 0.20)	171	This work
(2) Mainz, West Germany May - July 1972	0.80 ± 0.01 (± 0.16)	300	Schmidt (1974)
(3) Global background 1971 - 1974			
Northern hemisphere	0.584 ± 0.001 (± 0.027)		Schmidt (1978)
Southern hemisphere	0.552 ± 0.001 (± 0.010)		Schmidt (1978)

* The concentration unit is ppm of dry air volume. The quoted errors without and with parentheses represent the standard deviation of the average and the standard deviation of all the data, respectively.

** The number of the data in this work is that of the averages for the measurements made on the same days. The total number of all the individual measurements amounts to 702. The data from Mainz are given as six-hour averages of the continuous monitoring results (Schmidt, 1974). The number of the original measurements for which the averages of the global background levels were calculated, are not given by Schmidt (1978). From the given values of the two types of standard deviations, however, the numbers can be roughly estimated to be 100 or more.

bration errors.

Turkeltaub *et al.* (1964) have reported atmospheric He, Ne and H_2 concentrations by gas chromatography with a pre-enrichment technique for the He-Ne- H_2 fraction under a room temperature condition (Table 3). Their values for He and Ne differ from the accepted

values by 3% and 10% respectively, and are less accurate than present results by our simplified gas chromatographic method with no preliminary enrichment technique.

Hydrogen

The average of the atmospheric H_2 values in Matsuyama is 1.4 times as much as the northern hemispheric average of 0.584 ppm (Table 2), but very close to the average in Mainz of 0.80 ppm. Schmidt and Seiler (1970) noted that their continuous measurement of atmospheric H_2 on

Table 3. Comparison of atmospheric He and Ne determinations

He (ppm)	Ne (ppm)	Reference
5.239 ± 0.004	18.21 ± 0.04	Glückauf (1946)
5.23 ± 0.03	18.1 ± 0.08	Chackett <i>et al.</i> (1949)*
5.24 ± 0.004	18.18 ± 0.04	Glueckauf (1951)**
$5.4 \pm (0.25)$	$20.0 \pm (0.8)$	Turkeltaub <i>et al.</i> (1964)***
5.222 ± 0.017	—	Oliver <i>et al.</i> (1984)
5.20 ± 0.02	18.4 ± 0.1	This work

*This Ne value is not given in the original paper by Chackett *et al.* (1950) as Glueckauf (1951) cited. Their data on Ar, He and Ne in ground-level air are given in Chackett *et al.* (1949) as relative concentrations to $(N_2 + Ar)$. Therefore, these values for He and Ne are calculated by using the values for the atmospheric N_2 and Ar concentrations (Glueckauf, 1951).

**Compiled values accepted as the most reliable.

***Figures in parentheses represent one sigma errors for individual analyses, not the errors for means as for the other data. Such errors for the means are not given by Turkeltaub *et al.* (1964).

Fig. 4. Short-time fluctuation of the atmospheric H_2 concentration observed on October 10, 1983. The two-sigma analytical error for individual samples by our method is shown by the range of "Av. $\pm 2\sigma$ ". Note that six out of fifteen data points are outside this two-sigma error range.

the University of Mainz campus showed short time fluctuations due to motor traffic. Such fluctuations were also seen in our H₂ measurements as shown in Fig. 4: It was not unusual that the H₂ concentrations in air samples collected within 30 minutes were different by 50%. As listed in Table 2, the standard deviation of the atmospheric H₂ in Matsuyama amounts to 24%. This is much larger than the analytical error, 7% for an individual sample by our method. The large variation is quite comparable to the result from Mainz. The fluctuations in Matsuyama and Mainz are at least five times as much as the observed background

variations in the air on Atlantic and Pacific Oceans (Schmidt, 1978).

In the case of Mainz, Schmidt (1974) showed that the north and northeasterly winds from big industry regions with high traffic densities are accompanied by systematically higher H₂ concentrations than are the winds from rural areas. Such a correlation could not be found in Matsuyama, but as shown in Fig. 5, a relationship between the wind velocity and the atmospheric H₂ concentration can be seen. The H₂ concentration in the air on our sampling site seems to increase with decreasing wind velocity. The solid curve in Fig. 5 shows the trend esti-

Fig. 5. Correlation of the atmospheric H₂ concentration with the wind velocity. The H₂ data are the same as shown in Fig. 3. Information concerning precipitation is also given; solid circles represent the data obtained on the days with precipitation of 0.5 mm or more and open circles represent those obtained on the days with no precipitation or with precipitation less than 0.5 mm. The solid curve shows the average increasing trend of the atmospheric H₂ concentration with decreasing wind velocity. The point with the highest value of the daily mean wind velocity corresponds to the average for the four measurements made when a typhoon was approaching. The associated error bar shows the standard deviation of the four measurements on the stormy day. Note that this average on the stormy day is close to the global background level given by Schmidt (1978).

mated from the averages for the wind velocity less than 2.6m/s. Precipitation also seems to affect the increase in the atmospheric H_2 concentration. Linear correlation coefficients were calculated for the following groups of data points with the wind velocity less than 2.6m/s; (1) $r = -0.55$ for the data points of the days with precipitation of 0.5mm or more ($n=42$), (2) $r = -0.25$ for those with no precipitation or precipitation less than 0.5mm ($n=111$), and (3) $r = -0.40$ for all the data points ($n=153$). These results show that the negative correlation between the wind velocity and the H_2 concentration is more clearly seen on the days with precipitation than on those with no or very little precipitation.

wind velocity corresponds to the measurements made when a typhoon was approaching and wet air masses were moving from the Pacific Ocean. This value of 0.67 ± 0.14 ppm as the average for four measurements on the stormy day is probably close to the background H_2 level in Pacific coast areas of southwest Japan, and is not significantly different from the northern hemispheric background of 0.584 ± 0.027 ppm given by Schmidt (1978).

The H_2 concentration correlating with the wind velocity but not with the wind direction like the case of Mainz, is reasonable from the fact that our sampling site is located in a north-eastern part of the city of Matsuyama and surrounded by roads with relatively heavy motor traffic. The city itself is of a medium size with the population of about 400,000. There are no significant industries consuming vast amounts of fuel in this city and its vicinity. Therefore, the major source of H_2 is the exhaust gases from automobiles. It is known that such exhaust gases are enriched in H_2 , 1 - 5% by volume (Schmidt, 1974). Our measurements of H_2 in exhaust gases from an automobile engine gave a range of 0.8 - 3% by volume, in which higher values were obtained immediately after starting the engine. These values indicate that the H_2 concentrations in combustion gases of automobile gasoline engines are 10^4 times as high as the global background value. The H_2 sources

other than the exhaust gases are less important as suggested by the budget calculation of atmospheric H_2 by Schmidt (1974). In particular, H_2 of subsurface origins is least important: H_2 concentrations in bubble gases associated with artesian waters from fracture zones in this city are usually less than 10ppm (Kawabe, 1984/85). The soil gas survey around the Iyo Fault, which is an active fault located in the southwest of this city, does not suggest that the soil gases enriched in H_2 are being issued constantly from the active fault (Kawabe and Akaku, 1983).

The result shown in Fig. 5, therefore, is evidence for the process that the air polluted by H_2 -rich exhaust gases from automobiles is being diluted by less polluted air, in which the dilution does not occur effectively on rainy days with low wind velocities because advective and diffusive mixing is slow in such a weather condition.

CONCLUDING REMARKS

Trace atmospheric components, He, Ne and H_2 have been determined repeatedly over the last three years in Matsuyama by a simplified gas chromatographic method. The great simplicity of the analytical method without any preliminary enrichment of the trace components, made it easier to carry out many runs of the analyses including at least more than one hundred individual measurements of each component. The most probable values for the atmospheric He and Ne concentrations thus obtained have relatively small errors, and agree quite well with Glueckauf's (1951) values which have been believed for 40 years to be the most accurate.

The atmospheric H_2 concentration in Matsuyama shows a considerably large variation depending upon the wind velocity. The average value of H_2 concentration in Matsuyama is definitely higher than the global background value. The high and fluctuating H_2 concentration in the air is related to the air pollution by H_2 -rich exhaust gases from automobile engines. The city of Matsuyama is not located in the

highly industrialized area of this country, but the average level of the atmospheric H₂ is comparable to that reported from Europe ten years ago. This suggests that such air pollution by exhaust gases must be much more serious in larger cities of this country. Monitoring the atmospheric H₂ can provide information on the air pollution of this type.

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