Tellus (1978), *30,* 562–568

On the determination of sources of iron in atmospheric air by the Mössbauer technique

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(Manuscript received February 21; in final form August 14, 1978)

ABSTRACT

The Mössbauer effect was used for studying the iron concentration in atmospheric air. From the Mössbauer measurements at various temperatures it was possible to estimate the size of iron-containing particles, which together with the seasonal variations of iron concentration suggest that industrial air pollution contributes significantly to the concentration of iron in air. Under favourable conditions, iron of extraterrestrial origin was observed.

1. Introduction

During the last few years Mössbauer investigations of iron-containing atmospheric aerosols were conducted in our laboratory (Kopcewicz and Dzienis, 1971; Dzienis and Kopcewicz, 1973). It was shown that the Mössbauer effect can be successfully used for studies of the properties and concentration of iron in the air. This method was applied also in the investigations of iron concentration variations with air radioactivity due to nuclear explosions made in the atmosphere (Dzienis and Kopcewicz, 1973). The results of the measurements of iron concentration in the air indicated that the concentration varies considerably with time, site and meteorological conditions. It seems that studies of these variations combined with information on the size of iron-containing particles of aerosol may throw some light on the source of iron in the atmosphere.

In the present study the Mössbauer investigations of the seasonal variations of iron concentration in atmospheric air were continued and extended to include the samples collected from various sites in Poland. The results of these measurements combined with the data of the total air pollution and the evaluated size distribution of particles which contain iron suggest that industrial air pollution contributes considerably to the concentration of iron in the air. However, in favourable conditions, iron of extraterrestrial origin was observed.

2. Experimental

The samples used in the present study were prepared using membrane filters (Synpor II) which are usually used in the measurements of air radioactivity. Atmospheric air was pumped through each filter for 24 h, and the volume of air passed through each filter was measured by means of a gas meter. The filters were dissolved in acetone, evaporated, and the residue was pressed between two thin aluminium foils. Each sample used for Mössbauer measurements consisted of 15 filters obtained from the same site during 15 successive days. Thus, two samples per month were prepared for each site. In the present study the filters were collected at three sites in Poland in the periods given: Poznań (middle-west Poland) from June 1972 to March 1973, Wrocław (southwest Poland) from June 1972 to April 1974, and Kasprowy Wierch (a 1985-m-high summit in the Tatra mountains, southern Poland) from June 1972 to November 1974. The volume of air pumped through 15 filters was approximately 1000 m^3, 1700 m^3 and 1200 m^3 for Wrocław, Kasprowy Wierch and Poznań, respectively.

The samples were used in the Mössbauer

measurements as absorbers. The Mössbauer measurements were performed in a transmission geometry, using a constant acceleration Nokia Electronics Co. spectrometer with an 800-channel analyser. The source applied was ^{57}Co of 50 mCi activity in palladium foil. The measurements were carried out in the temperature range from 300 K to 75 K, using an Oxford Instruments Co. continuous flow CF-104 cryostat. The temperature of the sample was measured using a cryogenic linear temperature sensor, and the temperature stability, controlled by means of a precision temperature controller from Oxford Instruments Co., was better than ± 0.2 K for all temperatures.

The parameters of the Mössbauer spectra, such as linewidths, line positions, peak absorptions and the non-resonant background level, were computed by fitting the Lorentzian line shapes to the experimental data, using the least-squares method.

The air pollution was determined in μg/m^3, by weighing the amount of dust on each filter.

3. Results and discussion

The typical Mössbauer spectra obtained at room temperature for samples from Kasprowy Wierch consist of a quadrupole splitting doublet (QS) with $\Delta E_Q = 0.65$ mm/s (Fig. 1A). Fig. 2 shows several typical Mössbauer spectra obtained at room temperature for samples from Poznań. These spectra show a central QS doublet and beside it the second and fifth lines of the magnetic hyperfine splitting (hfs) sextet. The third and fourth lines are not separated from the QS doublet, and the first and sixth lines of the hfs sextet are placed out of the velocity range used.

The Mössbauer spectra obtained at room temperature for samples collected in Wrocław consist mainly of a central QS doublet of much larger intensity than that observed in the spectra from Kasprowy Wierch and Poznań. However, in several spectra obtained for the samples from Wrocław, magnetic hfs lines appear (Fig. 3). In this case four of the six lines of magnetic hfs could be observed, since the larger velocity range was used.

To calculate the concentration of iron in the sample it is necessary to establish in what chemical compound iron is contained. Such information can be obtained from Mössbauer measurements at low temperature. In the present study such measurements were performed in the temperature range from 300 K to 75 K. Typical results obtained for

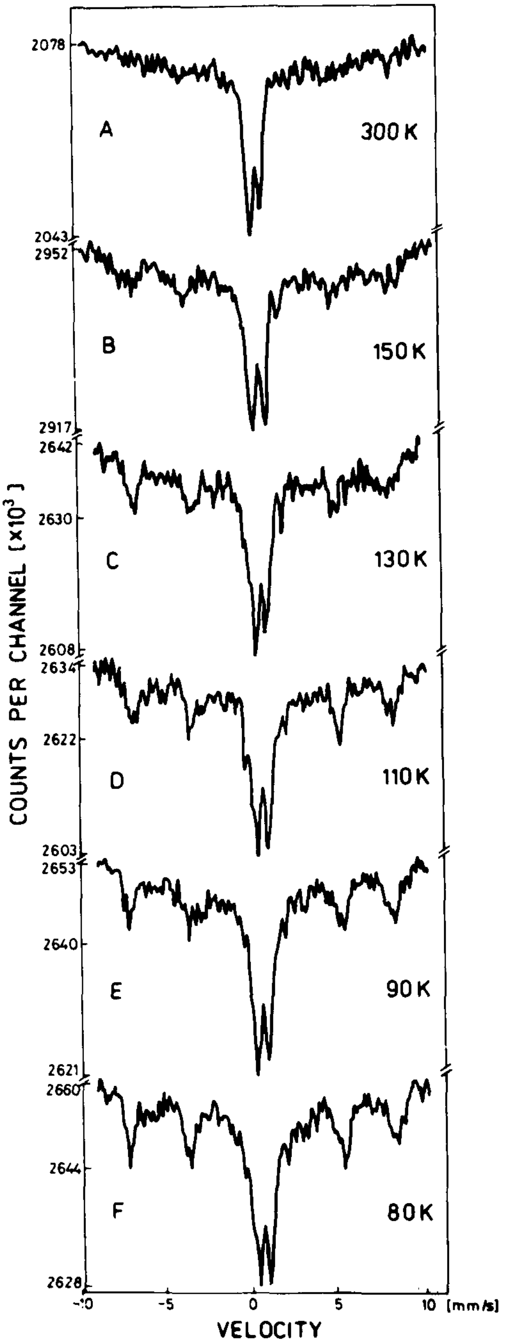

Fig. 1. Mössbauer spectra obtained as a function of temperature for the sample from Kasprowy Wierch.

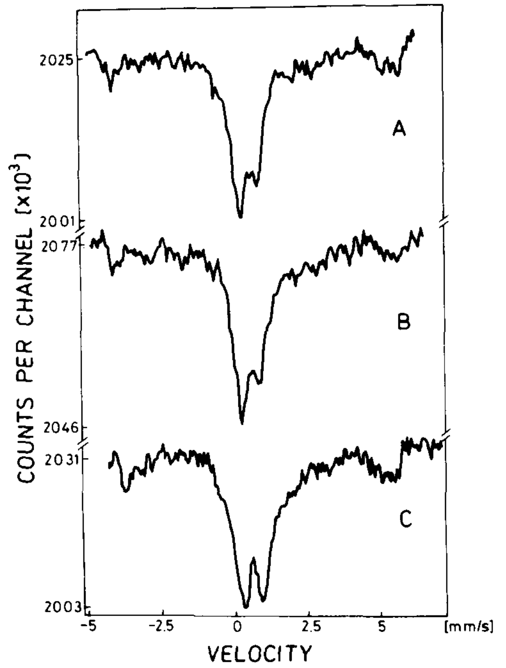

Fig. 2. Typical Mössbauer spectra obtained at 300 K for the samples from Poznań.

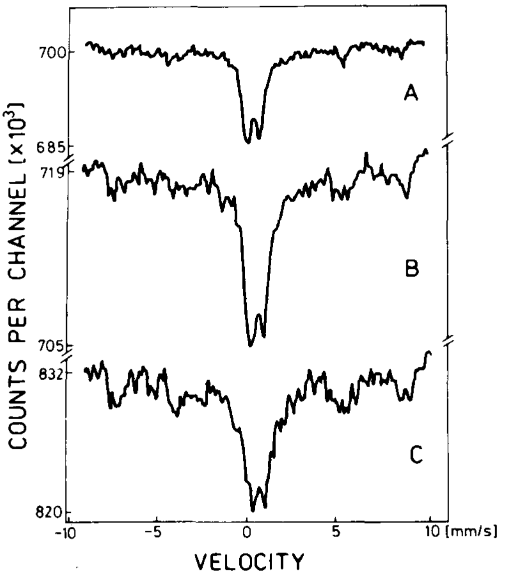

Fig. 3. Typical Mössbauer spectra obtained at 300 K for the samples from Wrocław.

the sample from Kasprowy Wierch are shown in Fig. 1. The Mössbauer measurements were carried out at several temperatures to observe the gradual changes of shape of the Mössbauer spectra, which allowed us to estimate the size distribution of iron-containing particles in the sample. In our previous paper (Kopcewicz and Dzienis, 1971) only the dominating size of iron-containing particles of aerosol was evaluated. As can be seen from Fig. 1, the decrease of the intensity of the QS doublet with decreasing temperature is accompanied by a simultaneous increase of the intensity of the magnetic hfs lines which appear in the spectra obtained below 150 K. The magnetic hyperfine field of H 520 kOe and the isomer shift of $\delta = 0.38$ mm/s, calculated for the magnetic fraction of the spectra, correspond exactly to the magnetic hf field and isomer shift of α-Fe_2O_3 (Kündig et al., 1966). Such a temperature behaviour of the spectra is typical of small superparamagnetic particles of α-Fe_2O_3 (Kündig et al., 1966). The disappearance of the hfs lines when the temperature is increased is due to fast relaxation of the magnetic moment of ultrafine particle, and the relaxation time is given by the formula:

$$\tau = \tau_0 \exp\left(\frac{KV}{kT}\right) \qquad (1)$$

where τ_0 is the frequency factor equal to 1.58×10^{-9} s for Fe_2O_3, K is the anisotropy constant found by Kündig et al. (1966) to be 4.1×10^4 erg/cm^3, V is the volume of the ultrafine particle, k is the Bolzmann constant, and T is the temperature. Fast relaxation of the magnetic moment of the particle leads to the collapse of the magnetic hfs spectrum to the QS doublet. When the relaxation time is shorter than the Mössbauer observation time, in our case equal to 2.5×10^{-8} s (the period of the precession of the nuclear magnetic moment of iron in the magnetic hyperfine field acting on the iron nuclei), then the spectrum consists of the QS doublet only. This shows that the particles are in the superparamagnetic state. For relaxation times longer than 2.5×10^{-8} s, the particles show ferromagnetic behaviour and magnetic hfs lines appear in the spectra. The temperature measurements show therefore that in our sample iron is contained in α-Fe_2O_3 in the form of ultrafine superparamagnetic particles.

From the results obtained for Kasprowy Wierch the dominating size of the Fe_2O_3 particles can be estimated. The radius of the particles was estimated

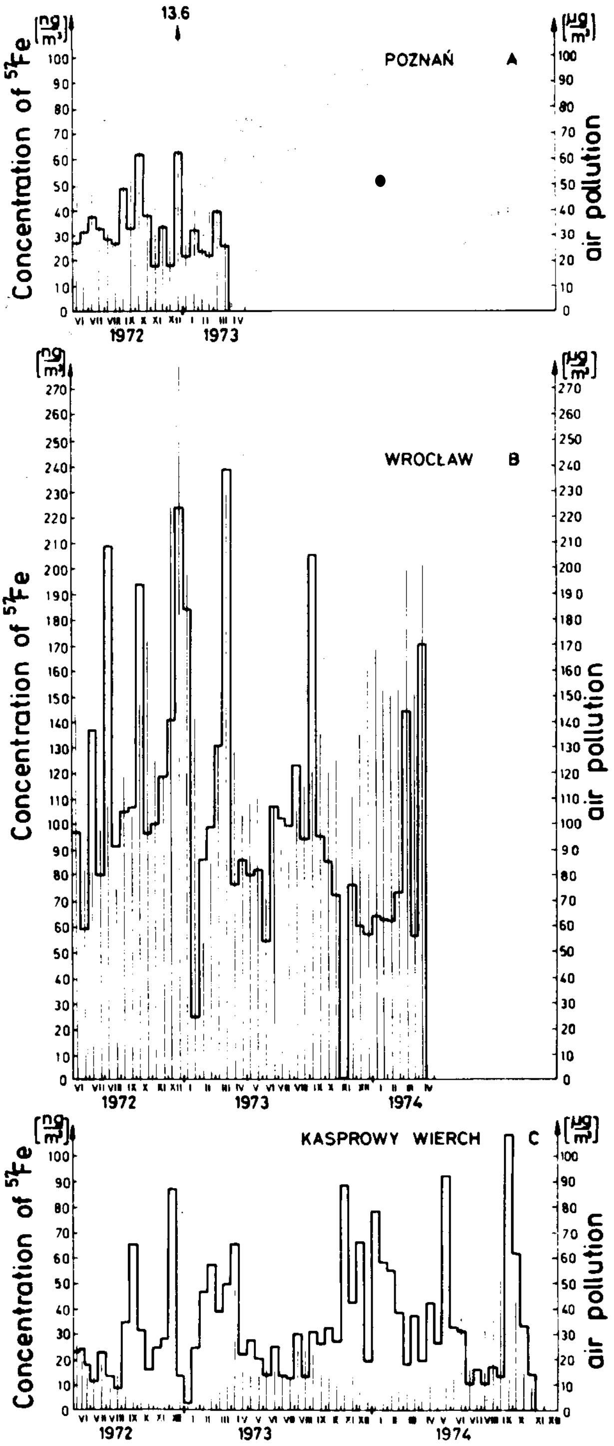

Fig. 4. Histogram of seasonal variations of ^{57}Fe concentration in air and the corresponding lines of air pollution obtained for Poznań (A), Wrocław (B) and Kasprowy Wierch (C).

from the spectrum obtained at 75 K in which 50% of Mössbauer absorption corresponds to the magnetic part of the spectrum and 50% to the non-magnetic part (QS doublet). In this case it can be assumed that the relaxation time is comparable to the observation time, and the volume of the particles can be evaluated from eq. (1). The radius of the dominating particles of Fe_2O_3 estimated in this way is about 55 Å.

In addition to the maximum, the cut-off of the size distribution of the iron-containing particles in the samples from Kasprowy Wierch was estimated. As can be seen from eq. (1) the relaxation time is comparable at 300 K to the observation time for the particle radius of 85 Å. So, for particles smaller than 85Å, superparamagnetic behaviour dominates at 300 K. Since in the spectra obtained for our samples from Kasprowy Wierch no magnetic hfs lines were observed at 300 K, one can infer that the maximum radius of Fe_2O_3 particles is larger than 55 Å but smaller than 85Å. This means that the size distribution of the iron-containing particles collected from Kasprowy Wierch is very narrow.

In the case of the samples from Poznań and Wrocław, the size distribution of the iron-containing particles is different. In the spectra in Figs. 2 and 3, the magnetic hfs lines corresponding to Fe_2O_3 appear beside the QS doublet at 300 K. Such a complex spectrum can be due to the coexistence of particles of two dominating sizes: small ones corresponding to the QS doublet (superparamagnetic fraction), and large ones contributing to the magnetic hfs lines. The radius of the larger particles estimated in a similar way as for the samples from Kasprowy Wierch is at least 135 Å.

In the present study the Mössbauer measurements were performed for 20 samples from Poznań, 61 samples from Kasprowy Wierch and 46 samples from Wrocław. In Fig. 4 the seasonal variations of ^{57}Fe concentration in the air obtained from Poznań (Fig. 4A), Wrocław (Fig. 4B) and Kasprowy Wierch (Fig. 4C) are presented. For all samples the concentration of ^{57}Fe in the sample was calculated from the experimental spectra using the "area method" (Hafemeister and Brooks Shera, 1966). This method was presented in detail in our previous papers (Kopcewicz and Dzienis, 1971; Dzienis and Kopcewicz, 1973). The method given by Hafemeister and Brooks Shera (1966) is normally used for calculations of the f-factor from the measured area under the Mössbauer lines. Since the density of the Mössbauer isotope in the sample is used when calculating f-factor, the content of the resonant isotope in the absorber can be inferred from the knowledge of the f-factor for the absorbing material. Comparing the theoretical absorption area with the experimentally measured absorption area and reversing the method given by Hafemeister and Brooks Shera (1966) one can evaluate the content of the Mössbauer isotope in the sample. Thus, the method described above of calculating iron content can be used only when a chemical compound which contains iron is established and when the f-factor for this compound is known or determined in another experiment. In every other case it is not possible to choose the proper value of the f-factor for the absorbing material. Since the systematic studies of the dependence of f-factor on the size of the particles are not presented in the literature, in the present paper the f-factor for bulk α-Fe_2O_3 was used in the calculations. However, it can be expected that f-factor corresponding to small particles will be smaller than that for bulk material. Use of the f-factor for bulk material affects the absolute value of iron concentration but does not affect the seasonal changes of iron concentration which are of main interest in this study. Since the volume of air which was pumped through each filter was known, it was possible to estimate the concentration of ^{57}Fe per cubic metre of air. The iron concentration data given in the literature are normally related to natural iron. In order to compare them with the data obtained by means of the Mössbauer technique, it is necessary to assume the natural abundance of iron in the sample (^{57}Fe constitutes 2.19% in natural iron) and calculate the concentration of natural iron. However, in the present paper the concentration of ^{57}Fe is used in the discussion of the results obtained. The statistical errors of the evaluation of iron concentration from our experiment due to the determination of the relevant Mössbauer parameters, such as line intensities, linewidths and the background, by fitting the Lorentzian lineshapes to the experimental spectra of the measured statistics, did not exceed 20%.

Fig. 4 presents the measured concentration of ^{57}Fe (histogram) and the total amount of air pollution collected for each sample. The industrial air pollution measured as dust concentration in the air, is by one order of magnitude larger for Wrocław than for Kasprowy Wierch. Comparison of the iron concentration for Poznań (Fig. 4A), Wrocław (Fig. 4B) and Kaprowy Wierch (Fig. 4C) suggests that the industrial air pollution has a noticeable influence on the content of iron in air. This is supported by the fact that the concentration of iron in air in Poznań and especially in Wrocław is much larger than for Kasprowy Wierch, and the increase of iron concentration in the two cities is accompanied by an increase of air pollution. As can be seen from the histogram for Kasprowy Wierch (Fig. 4C), the relationship between the concentration of iron in air and the total air pollution is inverse. The lowest concentration of iron was observed in summer, when air pollution was largest. Peaks of high concentration of ^{57}Fe were observed in mid-winter, when total air pollution is low. Since Kasprowy Wierch is a summit in the high Tatra mountains, where there are no sources of industrial air pollution in the vicinity, most of the dust registered for Kasprowy Wierch has been transported with air from Zakopane, a town situated at the foot of the mountains. There are also distant industrial sources of air pollution, but their emission is fairly stable all through the year, and nothing makes us think that the air pollution which is transported from distant sources is richer in iron in mid-winter than in summer. The relative content of iron, given as the ratio of iron to the total dust concentration, is much larger for the samples from Kasprowy Wierch than that for the samples from Poznań and Wrocław (Fig. 4).

The seasonal variations of dust concentration observed for the samples from Kasprowy Wierch (Fig. 4C) are connected with the fact that the intensity of turbulent and convective vertical transport of pollutants is much larger in summer than in winter, and therefore the registered amount of pollutants in winter is so low. These seasonal changes in the turbulent mixing influence the transport of pollutants from the nearest sources only. The fact that in winter, when air pollution is very low, peaks of iron concentration were observed, suggests that a considerable part of iron-containing particles collected at Kasprowy Wierch passes to the troposphere from the upper layers of the atmosphere. This suggestion is supported by the higher than for Poznań and Wrocław value of the relative content of iron in the samples from Kasprowy Wierch and the analysis of the variation of the size of iron-containing particles. The large concentration of iron observed in Poznań and Wrocław was accompanied by considerable changes of the shape of the Mössbauer spectra Figs. 1 and 2). These changes were caused by the different sizes of iron-containing particles, as was discussed above. It seems that the large iron-containing particles are of industrial origin and the small ones, as those collected at Kasprowy Wierch, are mostly of extraterrestrial origin. The possible source of the iron-containing particles collected at Kasprowy Wierch may be the systematic circulation between stratosphere and troposphere, since the peaks of iron concentration were observed at a time when the stratospheric flux to the troposphere is largest. Part of the iron-containing particles most probably enter the stratosphere as a result of the same stratosphere–troposphere exchange process. However, our results concerning the size of iron-containing particles suggest that at least a part of these particles may be of meteor origin.

As was stated above, the radius of the dominating particles containing Fe_2O_3 was determined at about 55 Å. Rosiński (1965) calculated that particles of 5 to 100 Å in diameter can be produced in the process of condensation of meteoric vapour. Meteors penetrate the atmosphere from space, and their interaction with the atmosphere produces deceleration and heating which lead to the evaporation of the meteor material. Subsequently, these vapours can condense. The size distribution of the condensed vapour particles depends on the competing rates of agglomeration and diffusion processes. These rates differ according to the initial particle concentration in the meteorite train, which varies with the meteorite size. The calculations of Rosiński (1965) performed for pressures corresponding to a height of 80–110 km above the earth's surface indicate that particles with average diameter of 10 to 60 Å can be formed in the first 10 s following the ablation of the meteorite. The agglomeration process which follows the condensation of the meteor's vapours, occurring under different conditions, leads to the formation of much larger particles with the diameter of the order of 10^{-4} cm, which approach the earth's surface. However, in our experiments, very small 55 Å particles were observed. This suggests that large particles formed in the agglomeration process may be composed of ultrafine particles. In our case the size of ultrafine particles should be understood as the radius of a magnetically ordered region which as a whole has a large magnetic moment. Such particles do not interact with the neighbouring regions by magnetic coupling; thus in the Mössbauer spectra no magnetic hfs lines are observed. However, such non-interacting superparamagnetic particles may be connected mechanically and in the process of transport of particles through the atmosphere can be considered as one large particle. Since the agglomeration process occurs under considerably different conditions than condensation of particles just after the ablation, the resulting large particles can be non-homogeneous. Such a form of particles approaching the earth's surface is strongly supported by our Mössbauer measurements.

It seems that Mössbauer investigations can be rewarding in the search for the sources of iron in air and may be useful in the studies of the properties of iron-containing particles of aerosols. Especially the investigation of samples from weakly polluted non-industrial regions should be very convenient for the study of the various processes occurring in the atmosphere. This would require, however, the analysis of numerous samples collected from different sites for a long period of time.

4. Acknowledgements

The authors are indebted to Dr I. Sosnowska for her interest in this study. Thanks are due to the Institute of Meteorology and Water Economy (Poland) for providing the filters and the necessary data concerning the pumping conditions and air pollution. The technical assistance of Mr S. Fijałkowski is acknowledged.

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SUMMARY

Эффект Мессбауэра был применен в исследованях концеентрации железа в атмосферном воздухе. На основании измерений эффекта Мессбауэра в разных температурах имеется возможность определения размеров частиц содержащих железо, что одновременно с сезонными изменениями концентрации железа даёт основание предполагать что загрязнения воздуха промышленного происхождения влияют на степень общего содержания железа в воздухе. В благоприятных условиях наблюдалось железо внеатмосферного происхождения.