Application of the Mössbauer effect in investigations of iron concentration variations with air radioactivity

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ABSTRACT

The Mössbauer effect was applied in the study of concentration of iron in the atmospheric air in relation to the air radioactivity. A correlation between air radioactivity due to nuclear explosions and concentration of iron was observed. The experiments were performed by observing the resonance absorption of 14.4 keV gamma rays from ^{57}Co by samples consisting of filters through which atmospheric air was pumped. The Mössbauer effect measurements were performed at room temperature. The concentration of iron-57 calculated using the "area method" varied from 0.54×10^{-2} $\mu g/m^3$ to 12.22×10^{-2} $\mu g/m^3$ in correlation with air activity variation from 0.05 pCi/m^3 to 9.16 pCi/m^3, depending on site and period of time. From the shapes of the Mössbauer spectra obtained it was inferred that iron appears in the Fe_2O_3 compound. The fresh fallout (high activity) contains a mixture of two dominating sizes of particles: small ones (~ 100 Å) in the form of ultrafine particles in the superparamagnetic state, and large ones, which contribute to the magnetic part of the spectra. The old fallout (low activity) contains small particles only. It testifies that large particles containing Fe_2O_3 originate mainly from the nuclear explosions.

1. Introduction

Investigations of atmospheric air radioactivity due to nuclear explosions performed in the atmosphere are of great importance for atmospheric physics. Of particular interest are the investigations of the particle properties of nuclear bomb debris which are important for many considerations concerning the radioactive fallout. The aspects of particle formation was extensively studied by many authors (cf. Storebø, 1965; Machta, 1961), but all these works concerned mainly the radioactive debris. The present study concentrates on atmospheric iron. It is shown that variations of the air radioactivity coincide with the changes of iron concentration in the atmospheric air which were studied by means of the Mössbauer effect. As it was shown in our recent paper (Kopcewicz & Dzienis, 1971) the Mössbauer effect can be successfully used for studying the properties and concentration of iron in the air.

2. Experimental

The Mössbauer effect measurements were performed using a conventional automatic spectrometer with constant velocity drive and a ^{57}Co in platinum source. The source and absorber were kept at room temperature. The samples were prepared in the same way as in our recent study (Kopcewicz & Dzienis, 1971) using the membrane filters usually used in the measurements of air radioactivity. The filters were collected at two sites in Poland: Warsaw (Central Poland) and Mikołajki (Mazury Lake District, Northern Poland), in different periods of time. Each sample consisted of several filters of similar activity obtained from the same site and period. The number of filters used in each sample varied from 6 to 15. The activity data for the filters were obtained from the State Institute of Hydrology and Meteorology. The measurements of air activity were performed by standard method. The β-activity of each filter

Table 1

Code	Site	Period	No. of filters	Average radioactivity [pCi/m³]
W1	Warsaw	May 1967	6	0.07
W2	Warsaw	April 1963	8	9.16
M1	Mikołajki	November/ December 1968	15	0.05
M2	Mikołajki	April 1967	15	0.11
M3	Mikołajki	December 1963	15	0.31
M4	Mikołajki	April/ Maj 1963	15	9.08

was measured using Geiger-Müller counter three days after sampling. The samples were used as absorbers. All details concerning the samples are summarized in Table 1. The samples from each site were numerated according to increasing air activity.

3. Results and discussion

The Mössbauer measurements were performed several times for each sample and the results obtained were fully reproducible. To improve the statistics and provide for the eventual errors due to the nonstability of the spectrometer during the long time measurements, the Mössbauer spectra obtained for each particular sample were added, i.e. the number of counts corresponding to each velocity channel of the consecutive spectra obtained for the same sample were added channel by channel. The parameters of the spectra were computed by the least squares method, fitting the Lorentzian shapes to the experimental data. The typical experimental and theoretical spectra are shown in Figs. 1 and 2. Figs. 1*a* and 1*b* presents the results obtained from samples W1 and W2, respectively. The spectrum obtained for sample W1 consists of two lines of the quadrupole splitting. The pattern of the spectrum, due to the presence of Fe_2O_3 in the form of ultrafine particles (about 100 Å) in superparamagnetic state, was discussed in details in our recent paper (Kopcewicz & Dzienis, 1971). The spectrum obtained for sample W2 shows a central unresolved doublet and, besides, the six lines of magnetic hyperfine structure (hfs). The positions of the lines of the magnetic fraction of the spectrum are very similar to those of the bulk $\alpha-Fe_2O_3$ spectrum lines. This indicates that the internal magnetic field in the sample is almost the same as in bulk $\alpha-Fe_2O_3$ (515 kOe at room temperature). According to the superparamagnetism model (Kneller, 1969; Künding et al., 1966) the shape of this spectrum can be interpreted in two ways:

(1) The ultrafine Fe_2O_3 particles in the W2 sample are larger than those contained in the W1 sample. This is based on the results obtained by Künding et al. (1966), who observed for 135 Å particles of Fe_2O_3 a spectrum which is quite similar to that obtained in our study.

(2) The sample W2 consists of two dominating sizes of Fe_2O_3 particles: "small" ones, of the size less than 100 Å, which contribute to the nonmagnetic part of the spectrum, and "large" ones of such size that at room temperature they show a ferromagnetic behaviour (>200 Å) and hence contribute to the magnetic part of the spectrum. A mixture of such particles in the sample can produce the spectrum of a shape very similar to that obtained for sample W2 (Fig. 1*b*). In our case the second explanation seems to be much more probable, but we shall return to that problem later.

Fig. 2 presents results obtained for samples M2 (Fig. 2*a*) and M4 (Fig. 2*b*) which are similar to those obtained for the samples W1 and W2, respectively. The spectrum obtained for sample M2 consists of a broad line of a linewidth almost three times larger than that obtained for sample W1. This suggests that the line observed for sample M2 is not a single one but consists of two lines of unresolved doublet of quadrupole splitting. This doublet could not be resolved because of the relatively large spread of the experimental points, connected with the small Mössbauer absorption observed, in view of the low concentration of iron in that sample (see Table 2). The quadrupole splitting estimated from the broadening of the absorption line is of the same magnitude as that observed for sample W1, which suggests that the average sizes of ultrafine particles Fe_2O_3 in samples M2 and W1 are similar.

Fig. 2*b* shows the Mössbauer spectrum obtained for sample M4. The spectrum consists of a nonmagnetic and magnetic part. The hfs lines are of smaller intensities than those for the sample W2, and only three lines are distinct.

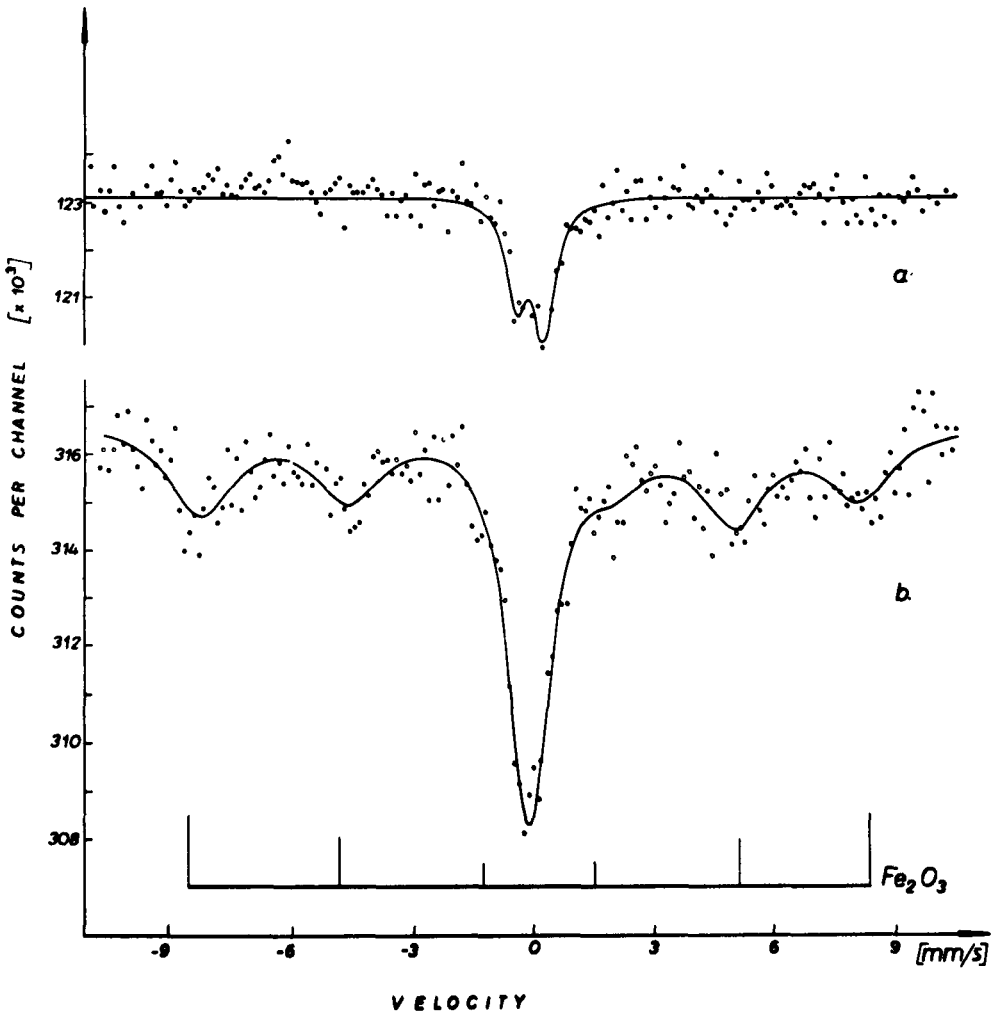

Fig. 1. Mössbauer spectra: (*a*) sample W1, (*b*) sample W2.

The shape of this spectrum can be interpreted in the same way as it was discussed above for sample W2. The shape of the spectrum obtained for sample M1 is identical to that for sample M2. In the case of sample M3 a spectrum of shape intermediate between those observed for samples M2 and M4 was obtained. From the Mössbauer measurements performed for all samples the concentration of iron in the air was calculated by the method given in our recent paper (Kopcewicz & Dzienis, 1971). Since the magnitude of the Mössbauer effect observed, described by so-called f-factor, depends on the concentration of the resonant isotope in the sample, the concentration of iron-57 isotope can be calculated from the knowledge of the f-factor for absorbing material. Hence we made use of the "area method" given by Hafemeister & Brooks Shera (1966) for the calculations of the f-factor, where the formula for the absorption area is:

$$A = \frac{\pi}{2} f \Gamma L(t) \tag{1}$$

where

$$t = n \sigma_0 f' \tag{2}$$

is the effective thickness of the absorber consisting of n atoms/cm² of the Mössbauer isotope, Γ

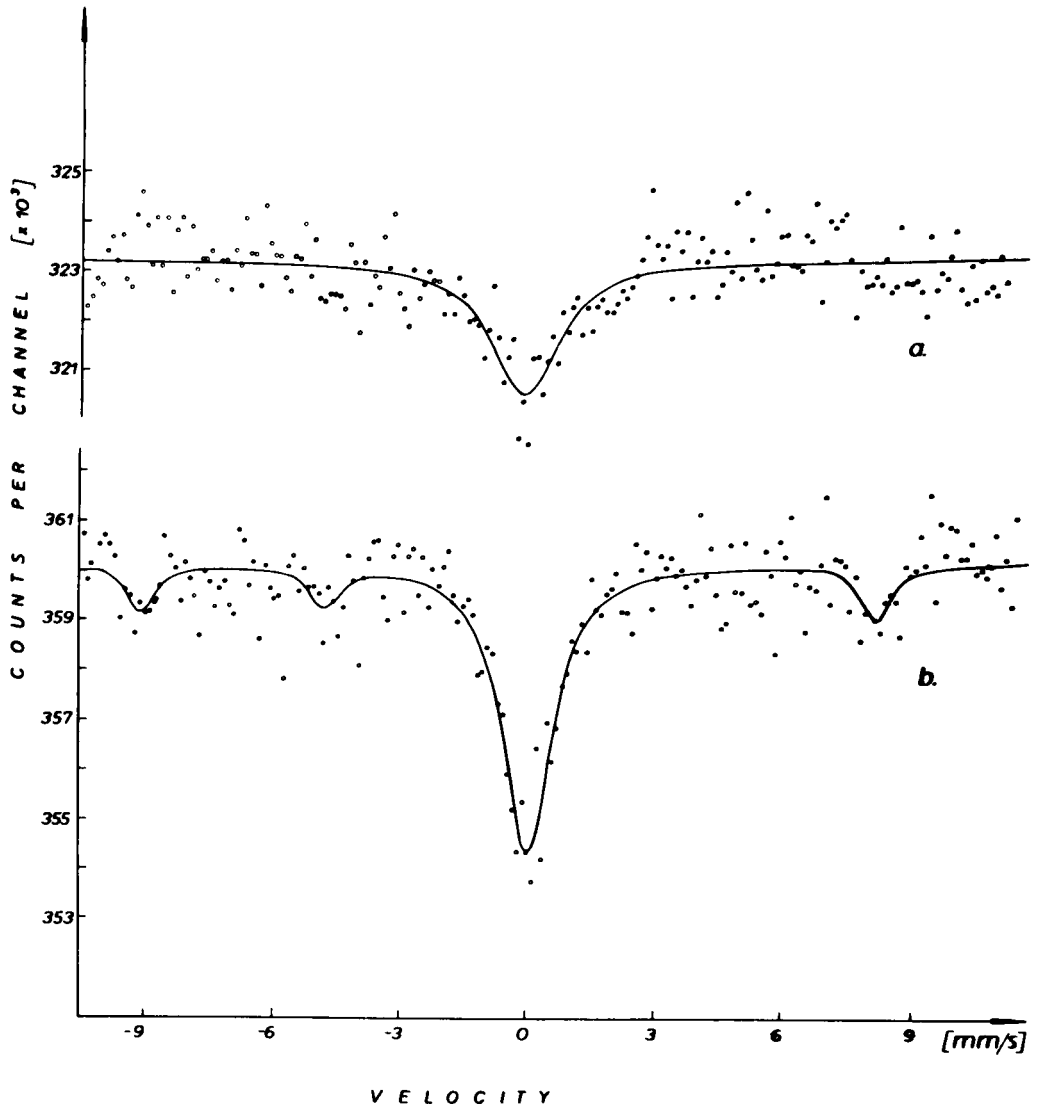

Fig. 2. Mössbauer spectra: (*a*) sample M2, (*b*) sample M4.

is the natural linewidth, σ_0 is the cross section for the resonant absorption of gamma rays, f and f' are the recoilless fractions for the source and absorber, respectively, $L(t)$ is a function of the absorber thickness which has been computed numerically and is given in the paper of Hafemeister & Brooks Shera (1966). Experimentally observed absorption under the Mössbauer spectrum consisting of i lines of Lorentzian shape

$$A = \frac{\pi}{2} \sum_{j=1}^{i} \Gamma_{j\,\mathrm{exp}}\, p_{j\,\mathrm{exp}} \tag{3}$$

where $\Gamma_{j\mathrm{exp}}$ are linewidths and $p_{j\mathrm{exp}}$ peak absorptions of the absorption lines.

By comparing eqs. (1) and (4) we obtained

$$L(t) = \frac{\sum_{j=1}^{t} \Gamma_{j\,\mathrm{exp}}\, p_{j\,\mathrm{exp}}}{f\Gamma} \tag{4}$$

and hence, using the results of Hafemeister & Brooks Shera (1966), the corresponding value of the effective thickness t.

So we finally get:

$$n = \frac{t}{\sigma_0 f'} \tag{5}$$

If the f'-factor for the absorber is known, it is possible to determine experimentally the concentration of the Mössbauer isotope, in our case ^{57}Fe, in the sample.

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 effect it is useful to assume the natural abundance of iron in the sample and calculate the concentration of natural iron. This assumption could be uncorrect in some cases, as it will be discussed below. The results of measurements and calculations are summarized in Table 2.

Table 2

Code	Average activity (pCi/m³)	Concentration of iron-57 (μg/m³)	Concentration of natural iron (μg/m³)	Shape of the spectrum
W1	0.07	3.14×10^{-2}	1.44	nm[a]
W2	9.16	12.22×10^{-2}	5.66	nm + mhfs[a]
M1	0.05	0.54×10^{-2}	0.24	nm
M2	0.11	1.28×10^{-2}	0.58	nm
M3	0.31	1.58×10^{-2}	0.72	nm + mhfs
M4	8.08	2.64×10^{-2}	1.20	nm + mhfs

[a] nm = nonmagnetic, mhfs = magnetic hyperfine structure.

As can be seen from Table 2 the correlation between the average activity of the air and the concentration of iron is evident. For the samples both from Warsaw and Mikołajki an increase of the air activity is accompanied by an increase of iron concentration and the appearence of magnetic lines in the spectrum. The large activities of the air observed in April 1963 were cuased by the extensive nuclear explosions performed in the atmosphere at that time. It is known that the casing of the bomb, weighting several tons, is generally made of iron. During the explosion the bomb material vaporizes, and appears in a warm mass which rises rapidly through the atmosphere (Storebø, 1965). As it cools down the particles are formed in a condensation process. The explosions are different in nature and size, so, the conditions under which the particles are formed vary widely. The substances originating from the early stages of some decay chains are gaseous or volatile, and particles which start to grow very early or very late in the condensation phase may have an increased or decreased content of certain isotopes. Substantial differences in particle properties may also arise from that the bombs may be larger or smaller, and hence the cooling and later condensation of the particles may proceed less or more rapidly. As a result differences in particle size and composition should be anticipated. Iron can therefore occur in the form of particles of different sizes. The particles large, from the superparamagnetic point of view, contribute to the magnetic lines of the spectrum and cause an increase of the concentration of iron in the air (see Table 2). The appearence of large particles of iron is confirmed by the fact that the intensity of the magnetic fraction in the spectrum decreases in the course of relatively short time. This effect can be followed for the Mikołajki samples. As can be seen from Table 2, the decrease of iron-57 concentration from 2.64×10^{-2} μg/m³ obtained for sample M4 to 1.58×10^{-2} μg/m³ for sample M3, observed in the course of eight months, is mainly due to the decrease of the intensity of the magnetic fraction of the spectrum. This is connected with a fairly rapid fallout of large particles. This picture is consistent with our explanation given above. The decrease of the intensity of the superparamagnetic doublet observed, is due also to the fallout of small ultrafine particles, but this process is much slower than that for large particles and can be observed after a much longer period of time. This fact can be illustrated by the changes of iron concentration observed for samples M3 and M1. The decrease from the value 1.58×10^{-2} μg/m³ to 0.54×10^{-2} μg/m³ for samples M3 and M1, respectively, is comparable to the changes of concentration of iron observed for samples M3 and M4, but occurs in much longer time, i.e. after several years. It also suggests that large particles originate mainly from the nuclear explosions.

The second possibility of the concentrations of iron, as determined by the Mössbauer effect, being higher is the enrichment of natural iron in ^{57}Fe isotope. During a nuclear explosion, when the neutron flux is very high, such a process can occur in the ^{56}Fe$(n, \gamma)^{57}$Fe reaction. In this case the assumption of the natural abundence of iron in the sample is not valid.

The absolute values of concentration of iron obtained for Warsaw are larger than those for

Mikołajki owing to the higher industrial pollution background. A detailed consideration of the effect of industrial pollution on the concentration of iron in the air would require an analysis of numerous samples taken from different sites, account being taken of the meteorological conditions.

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REFERENCES

Hafemeister, D. W. & Brooks Shera, E. 1966. Calculations of the Mössbauer absorption areas for thick absorbers. *Nucl. Instr. Methods 41*, 133–134.

Kneller, E. 1969. Fine particles theory. In *Magnetism and Metallurgy* (ed. A. Berkowitz and E. Kneller), pp. 365–471. Academic Press, New York and London, 1969.

Kopcewicz, M. & Dzienis, B. 1971. Mössbauer study of iron in atmospheric air. *Tellus 23* (2), 176–181.

Kündig, W., Bömmel, H., Constabaris, G. & Lindquist, H. R. 1966. Some properties of supported small α-Fe_2O_3 particles determined with the Mössbauer effect. *Phys. Rev. 142*, 327–333.

Machta, L. 1961. A survey of information on meteorological aspects of world-wide fallout. In *Meteorological factors influencing the transport and removal of radioactive debris* (ed. W. Bleeker, Tech. Note No. 43, WMO—No. 111 TP. 49), pp. 3–30.

Storebø, P. B. 1965. On particles formation in nuclear bomb debris. In *Meteorological aspects of atmospheric radioactivity* (ed. W. Bleeker, Tech. Note No. 68, WMO—No. 169, TP. 83), pp. 1–26.

РЕЗЮМЕ

Эффект Месбауэра был применен в исследованиях концентрации железа в атмосферном воздухе. Установлено зависимость между радиоактивностю воздуха вызваной ядерными взрывами и содержанием железа в атмосфере. Опыты производились путем исследования 14,4 кев γ-лучей ^{57}Co употребляя пробы состоящие из фильтров, через которые пропускался атмосферный воздух. Измерения производились в комнатной температуре. Концентрация железа-57 вычислена при помощи «метода поля» изменялась от $0{,}54 \times 10^{-2}$ $\mu г/м^3$ до $12{,}22 \times 10^{-2}$ $\mu г/м^3$ что зависело от изменений активности воздуха от 0,05 пCi/$м^3$ до 9,16 пCi/$м^3$ а также от времени и места сбора пробы. На основании формы месбауэровских спектров установлено что железо выступает в составе Fe_2O_3. Свежое выпадение (высокая активность) содержит смесь частиц в двух доминирующих величинах: ультра малых (~ 100 Å) в суперпарамагнитном состоянии и больших, которые вызывают появление магнитной части спектра. Старое выпадение (низкая активность) содержит только малые частицы что свидетельствует о том, что большие частицы, содержащие Fe_2O_3, являются, главным образом, следствием ядерных взрывов.