

OCCUPATIONAL EXPOSURE ASSESSMENT FOR CRYSTALLINE SILICA DUST: APPROACH IN POLAND AND WORLDWIDE

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Abstract

Crystalline silica is a health hazard commonly encountered in work environment. Occupational exposure to crystalline silica dust concerns workers employed in such industries as mineral, fuel-energy, metal, chemical and construction industry. It is estimated that over 2 million workers in the European Union are exposed to crystalline silica. In Poland, over 50 thousand people work under conditions of silica dust exposure exceeding the occupational exposure limit. The assessment of occupational exposure to crystalline silica is a multi-phase process, primarily dependent on workplace measurements, quantitative analyses of samples, and comparison of results with respective standards. The present article summarizes the approaches to and methods used for assessment of exposure to crystalline silica as adopted in different countries in the EU and worldwide. It also compares the occupational limit values in force in almost 40 countries. Further, it points out the consequences resulting from the fact that IARC has regarded the two most common forms of crystalline silica: quartz and cristobalite as human carcinogens. The article includes an inter-country review of the methods used for air sample collection, dust concentration measurements, and determination of crystalline silica. The selection was based on the GESTIS database which lists the methods approved by the European Union for the measurements and tests regarding hazardous agents. Special attention has been paid to the methods of determining crystalline silica. The author attempts to analyze the influence of analytical techniques, sample preparation and the reference materials on determination results. Also the operating parameters of the method, including limit of detection, limit of quantification, and precision, have been compared.

Key words:

Crystalline silica, Quartz, Occupational exposure assessment, Limit value, X-ray diffraction, Infrared spectrophotometry

INTRODUCTION

Silica (silicon dioxide) is a common name of several minerals and an amorphous substance. Silicon and oxygen that make silica are the two most widespread elements in the Earth's crust. In the natural environment, silica is primarily found either in the evidently crystalline or cryptocrystalline form, and sometimes in an amorphous form. A common crystalline form of SiO_2 is quartz, the most thermodynamically stable polymorph under ambient conditions. The forms crystallizing at higher temperatures, namely cristobalite and tridymite, are much more scarce. Still less common forms are moganite and melanophlogite, as well as the high-temperature and high-pressure polymorphs:

coesite, keatite and stishovite, practically not encountered in nature. The cryptocrystalline forms include chalcedony, agate, flint, jasper and others. All the crystalline forms of silica are referred to as "free crystalline silica" [1].

Quartz makes up 12% of the lithosphere and is an important element of all kinds of rocks: igneous, sedimentary, and metamorphic, as well as of the soils. It is almost the only component of solid rocks, such as sandstone or quartzite, loose rocks, and sand and gravel, that are the basic source of silica in industry. Quartz is characterized by high chemical resistance; it can be dissolved only in hydrofluoric acid and, at high temperatures, also in hydroxide and alkaline carbonates. Moreover, it has a particularly

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high hardness — 7 on the Mohs scale, and a high melting point — 1713°C. Its ubiquity in the natural environment as well as the specific physicochemical properties make quartz widely used in the industry. In Poland, apart from quartzite and sandstone, almost 4 million tons of quartz sand and silica sand are mined every year [2].

Crystalline silica in work environment has long been known to be harmful to human health. Long-term breathing of fine dust particulates of the respirable fraction is associated with the development of silicosis. Exposure to silica is one of the etiological factors of coal miners' pneumoconiosis. Moreover, it can contribute to an increased incidence rate of respiratory diseases such as chronic bronchitis and pulmonary emphysema, and of immunological disorders and chronic kidney dysfunction [3–5].

Occupational exposure to crystalline silica refers mainly to mining, construction, agriculture, and industry. Exposure to quartz dust can be primarily encountered at the following worksites:

- in quarries, coal mines and raw mineral mines of chemical resources and metal ores;
- in ferrous and non-ferrous metal industry e.g. zinc and aluminum;
- in glassware plants manufacturing architectural glass, domestic glassware, lighting glass, optical glass, laboratory glassware, and glass fibers;
- in whiteware ceramics, sanitary and technical ware, and faience industry;
- in plants producing ferrosilicon, other silicon alloys and metallic silicon;
- in building stone and building material works (concrete, plaster work, mortar);
- at industrial and housing construction sites;
- at road and tunnel construction sites;
- in refractory and abrasive material works;
- in production of chemicals for chemical industry: sodium silicate, silicones, sealants and binders, paints (ceramic color), rubber, fertilizers and pesticides;
- in electric power stations and heating plants using coal;
- in workshops processing precious and semiprecious silica stones;

— in agriculture and gardening.

Exposure to other forms of crystalline silica: cristobalite and tridymite usually takes place under conditions of technological processes involving roasting at temperatures of at least 1000°C, or roasting of raw materials containing quartz, kaolin or amorphous silica (e.g. diatomaceous earth, siliceous earth, and diatomites). Cristobalite dust exposure may occur in the plants manufacturing refractories, abrasive materials, ceramic ware and faience, paints, and catalysts for chemical industry, as well as pesticides and fertilizers when natural silica materials are used as fillers.

The workers exposed to the highest concentrations of crystalline silica dust include:

- workers employed to bore tunnels;
- workers performing tasks involving crushing, cutting, grinding or drilling rock and building materials (e.g. concrete) in mines, as well as in rooms with inefficient ventilation;
- workers performing tasks related to abrasive cleaning of large surfaces, with the use of sand;
- workers involved in pouring liquid silica materials;
- workers cleaning castings and repairing high-temperature furnaces;
- workers performing dry processing of ceramic ware, refractories and abrasive products [3,6,7].

In the European Union, the number of workers exposed to crystalline silica, except for coal miners, is estimated to be over 2 million [8], and the data collected for many years at the national databases: COLCHIC in France [9] and MEGA in Germany [10], provide evidence that the determination of crystalline silica is one of the most prevalent analyses conducted in work environment. In Poland, according to the statistics of GUS (Central Statistical Office), over 50 thousand people [2] are exposed to industrial dust at levels exceeding occupational exposure limits, which are the conditions conducive to the development of lung fibrosis. The actual number of thus exposed workers is higher since the GUS statistics do not include enterprises employing less than 10 workers.

APPROACH TO OCCUPATIONAL EXPOSURE ASSESSMENT FOR CRYSTALLINE SILICA DUST

The assessment of occupational exposure to chemical agents harmful to human health, including free crystalline silica, is a multi-phase process. At the initial stage, it consists in collecting information on the technological processes and organization of work in a given workplace, and identifying the potential sources of exposure. Then comprehensive field measurements are carried out to determine the concentration of a given agent, evaluate the hygienic conditions in workplace and compare them with relevant occupational exposure limits. In Poland, like in many other European countries, this process of occupational exposure assessment is conducted according to the general strategy for measurements of workplace hazards, and the guidelines included in the PN-EN-689:2002 standard [11]. On the other hand, the exposure assessment criteria, defining also the necessary testing procedures, include the limit values for the concentration of hazardous substances.

LIMIT VALUES FOR WORKPLACE CONCENTRATIONS OF CRYSTALLINE SILICA DUST

No uniform international system of setting the limit values for workplace concentrations of hazardous agents has as yet been established. Moreover, there is even no common definition of the limit value or of the safety level with respect to occupational exposure. The setting of the limit values is based on two levels: the safety level (assumed to protect all the exposed workers against health effects) and the border level (assumed to provide safety to almost all the exposed workers except for individuals with increased susceptibility to adverse effects of a given hazard). In practice, the limit values are implemented mostly on the basis of a compromise between the health requirements and the technical possibility of satisfying them.

Leading organizations dealing with workers' health protection, like the American Conference of Governmental Industrial Hygienists (ACGIH) and the National

Institute for Occupational Safety and Health (NIOSH) in the USA, have worked out documentation and proposed standards based on analyzing the outcomes of the most recent research reported in world literature. The limit values recommended by these organizations make a reference point for defining the hygienic standards in other countries. Also the European Union has decided to develop a list of standards [12–14]. This example was followed by 50 countries, including Poland [15]. Table 1 presents the limit values for crystalline silica in workplace as promoted by ACGIH and NIOSH, as well as the standards adopted in more than 30 countries all over the world.

The standard values for crystalline silica are expressed in two ways. The most common method (used by ACGIH and NIOSH) involves quoting the limit mass of respirable fraction of crystalline silica dust or its polymorphs in 1 m³ of air collected in workplace, in relation to an 8-hour or 10-hour work shift and a 40-hour work week. Another method involves limiting the concentration of dust with a specified range of percentage content of crystalline silica, or calculating the standard value according to a given formula, taking into account the proportion of quartz or free crystalline silica. The limit values for crystalline silica (100%) concentrations, defined in such a way, refer not to a single standard value expressed as the respirable dust mass in air volume, but they fall within a concentration range. In addition to the standards regarding respirable dust and based on the critical effects of exposure: fibrosis and silicosis, some countries, e.g. the USA (the legally-binding standards of the Occupational Safety and Health Administration (OSHA) and the standards in force in California), as well as Denmark, Greece, India, the Canadian province of Alberta, Norway, Hungary, Thailand, and Poland have also developed the standards for the total dust that consider the irritant effect of silica on the respiratory tract. On the other hand, such countries as Russia and Lithuania have decided to adopt the standard values for total dust concentrations only with respect to quartz and cristobalite exposure. The few existing limit values for crystalline silica concern the short-term exposure concentrations.



Table 1. Occupational exposure limits for free crystalline silica

No.	Organiza- tion/ country	Exposure limit and interpretation	Limit values			Value range in refer- ence to 100% SiO ₂	Carcino- genicity remarks	Year of introduc- tion /publica- tion	Informa- tion source
			Crystalline silica form	Dust fraction	Limit value [mg/m ³]				
1	ACGIH, USA	TLV — Threshold Limit Value (TWA-8h, 40-h week) ¹	crystalline silica: α-quartz cristobalite	respirable	0.025	–	A2	2006	16, 17
2	NIOSH, USA	REL — Recom- mended Exposure Limit (TWA-10h, 40-h week)	quartz cristobalite tridymite	respirable	0.05	–	Ca (NIOSH)	1974 (quartz)	4, 18
3	European Union	IOELV — Indicative Occupational Ex- posure Limit Value (TWA-8h)	crystalline silica	IOELV for crystalline silica not established					12, 13, 14
4	Argentina	CMP — Concen- tración Máxima Permisible (TWA- 8h, 40-h week)	quartz cristobalite tridymite	respirable	0.05	–	quartz: A2	2003	19
5	Australia	Exposure Standard (TWA-8h)	quartz cristobalite tridymite	respirable	0.1	–	no	2004	20
6	Austria	MAK — Maximale Arbeitsplatz- konzentrationen (TWA-8h, 40-h week)	quartz cristobalite tridymite	respirable	0.15	–	no	1992	21, 22
7	Belgium	VLEP — Valeurs Limites d'Exposition Professionnelle	quartz cristobalite tridymite	respirable respirable	0.1 0.05	– –	no no	1995	21, 23
8	Bulgaria	Concentration limit (TWA-8h)	quartz cristobalite tridymite	respirable	0.07	–	no	2003	24
9	Canada:								
	Quebec	VEMP — Valeur D'Exposition Moy- enne Pondérée (TWA-8h)	quartz cristobalite tridymite	respirable respirable	0.1 0.05	–	C2	1996	21, 25
	Alberta	OEL — Occupation- al Exposure Limit (TWA-8h)	quartz cristobalite tridymite cristobalite tridymite	respirable total dust respirable total dust	0.1 0.3 0.05 0.15	–	nd	1988	26

Table 1. Occupational exposure limits for free crystalline silica — cont.

No.	Organiza- tion/ country	Exposure limit and interpretation	Limit values			Value range in refer- ence to 100% SiO ₂	Carcino- genicity remarks	Year of introduc- tion /publica- tion	Informa- tion source
			Crystalline silica form	Dust fraction	Limit value [mg/m ³]				
	British Colum- bia	OEL — Occupa- tional Exposure Limit (TWA-8h)	α-quartz cristobalite	respirable	0.025	–	A2	2006	27
10	Chile	LPP — Limite Per- misible Ponderado	quartz cristobalite tridymite	respirable respirable	0.08 0.04	–	no	1992	28
11	Czech Republic	OEL — Occupational Exposure Limit	quartz cristobalite tridymite	respirable	0.1	–	nd	nd	29
12	Denmark	LV — Limit Value	quartz	respirable	0.1	–	K	1988	21, 30
				total dust	0.3	–	no		
			cristobalite	respirable,	0.05	–	K		
			tridymite	total dust	0.15	–	no		
13	Estonia	Piirnormid (TWA-8h)	quartz cristobalite tridymite	respirable respirable	0.1 0.05	–	no	1998	31
14	Finland	HTP — Haitalliseksi Tunnetut Pitoisuudet (TWA-8h)	quartz cristobalite tridymite	respirable respirable	0.2 0.1	–	nd	1993	21, 32
15	France	VME — Valeur Limite de Moyenne d'Exposition (TWA-8h, 40-h week)	quartz cristobalite, tridymite	respirable respirable	0.1 0.05	–	no	1997	33
16	Germany	MAK — Maximale Arbeitsplatzkon- zentrationen	quartz cristobalite tridymite	no standard — employers are obliged to minimize exposure			MAK-1	nd	18, 29
17	Great Britain	WEL — Workplace Exposure Limit (TWA-8h)	crystalline silica	respirable	0.1	–	no	2006	34
18	Greece	OEL — Occupational Exposure Limit	quartz cristobalite, tridymite	respirable respirable	0.1 0.05	–	nd	nd	29
19	Hungary	Megengedett koncentráció	quartz cristobalite tridymite	respirable	0.1	–	nd	2000	36
20	India	PLE — Permissible Limit of Exposure	quartz dust containing free silica	total dust respirable total dust	6 10 <u>%quartz + 2</u> 30 <u>%quartz + 3</u>	0.03–0.1 0.075–0.3	nd	1987	37



Table 1. Occupational exposure limits for free crystalline silica — cont.

No.	Organiza- tion/ country	Exposure limit and interpretation	Limit values			Value range in refer- ence to 100% SiO ₂	Carcino- genicity remarks	Year of introduc- tion /publica- tion	Informa- tion source
			Crystalline silica form	Dust fraction	Limit value [mg/m ³]				
21	Ireland	OEL — Occupa- tional Exposure Limit	quartz cristobalite, tridymite	respirable	0.05	–	nd	nd	29
22	Italy	TLV — Threshold Limit Value	quartz cristobalite, tridymite	respirable	0.05	–	nd	nd	29
23	Japan	OEL-C — Occu- pational Exposure Limit Ceiling	crystalline silica	respirable	0.03	–	group 1	2006	38
		OEL — Occupa- tional Exposure Limit	dusts < 10% of free silica	respirable total dust	1 4	0.01–0.1 0.04–0.4	– –		
24	Lithuania	AER — Aroda Ekkspozīcijas robežvērtība (TWA-8h, 40-h week)	dusts > 70% of total dust	crystalline SiO ₂	1	0.7–1.0	nd	nd	39
			dusts from 10% to 70% of crys- talline SiO ₂		2	0.2–1.4			
			dusts from 2% to 10% of crys- talline SiO ₂		4	0.08–0.4			
25	Luxemburg	Valeur Limite	quartz cristobalite tridymite	respirable	0.15	–	nd	nd	29
26	Mexico	OEL — Occupa- tional Exposure Limit (TWA)	quartz cristobalite, tridymite	respirable respirable	0.1 0.05	–	nd	2004	40, 41, 42
27	New Zealand	Workplace Expo- sure Standard (TWA-8h)	quartz cristobalite, tridymite	respirable respirable	0.2 0.1	–	A2	2002	43
28	Norway	OEL — Occupa- tional Exposure Limit (TWA)	α-quartz	respirable	0.1	–	K	1994	21, 44
				total dust	0.3				
			cristobalite	respirable	0.05				
29	Portugal	OEL — Occupa- tional Exposure Limit	tridymite	total dust	0.15				
			quartz cristobalite, tridymite	respirable	0.05	–	nd	nd	29
30	RPA: DOL (Depart- ment of Labour)	OEL-CL — Occu- pational Exposure Limit — control limit (TWA)	quartz	respirable	0.4	–	no	1995	45

Table 1. Occupational exposure limits for free crystalline silica — cont.

No.	Organiza- tion/ country	Exposure limit and interpretation	Limit values			Value range in refer- ence to 100% SiO ₂	Carcino- genicity remarks	Year of introduc- tion /publica- tion	Informa- tion source
			Crystalline silica form	Dust fraction	Limit value [mg/m ³]				
	DME (Depart- ment of Minerals and En- ergy)	OEL — Occupa- tional Exposure Limit	quartz cristobalite tridymite	respirable	0.1	–	no	2002	
31	Russia	OEL — Occupa- tional Exposure Limit — TWA	quartz	total dust	1	–	nd	2003	40, 41
		STEL — Short- Term Exposure Limit			3				
		STEL — Short- Term Exposure Limit	cristobalite	total dust	1				
32	Slovakia	NPHV — Najvyššie Pripustné Hodnoty Vystavenia	quartz cristobalite tridymite	respirable	0.1	–	quartz: Cc	2002	46
33	Slovenia	OEL — Occupa- tional Exposure Limit	quartz cristobalite tridymite	respirable	0.15	–	nd	nd	29
34	Spain	VLA-ED — Valore Limite Ambient- ales-Exposición Diaria (TWA-8h; 40-h week)	quartz cristobalite tridymite	respirable respirable	0.1 0.05	–	no	2003	47
35	Sweden	NGV — Nivågrän- svärde (TWA-8h)	quartz cristobalite tridymite	respirable respirable	0.1 0.05	–	no	1996	48
36	Switzer- land	VME — Valeur Limite de Moyenne d'Exposition (TWA-8h, 42-h week)	quartz cristobalite tridymite	respirable	0.15	–	Cc	nd	49
36	Thailand	TWA	quartz cristobalite tridymite	respirable	10	–	nd	1993	40, 41, 42
			quartz	total dust	30				
38	The Nether- landes	MAC — Maximaal Aanvaarde Concen- traties (TWA-8h)	quartz cristobalite tridymite	respirable	0.075	–	Cc	1996	35



Table 1. Occupational exposure limits for free crystalline silica — cont.

No.	Organiza- tion/ country	Exposure limit and interpretation	Limit values			Value range in refer- ence to 100% SiO ₂	Carcino- genicity remarks	Year of introduc- tion /publica- tion	Informa- tion source
			Crystalline silica form	Dust fraction	Limit value [mg/m ³]				
39	United States								
	OSHA	PEL — Permis- sible Exposure Limit (TWA-8h, 40-h week)	dust containing quartz	respirable	10 mg/m^3 $\% \text{SiO}_2 + 2$	0.03–0.1	no	1971	21, 50
				total dust	30 mg/m^3 $\% \text{SiO}_2 + 2$	0.09–0.3			
			dust containing cristobalite, tridymite	respirable	$\frac{1}{2}$ of the value for quartz	0.015–0.05	no	1978	
				total dust	$\frac{1}{2}$ of the value for quartz	0.045–0.15			
	California	PEL — Permis- sible Exposure Limit	quartz	respirable	0.1	–	no	nd	51
				total dust	0.3				
			cristobalite, tridymite	respirable	0.05				
	Michigan	EL — Exposure Limit (TWA-8h, 40-h week)	quartz	respirable	0.1	–	no	nd	52
			cristobalite, tridymite	respirable	0.05				
	Minnesota	PEL — Permis- sible Exposure Limit (TWA-8h)	quartz	respirable	0.1	–	no	nd	53
			cristobalite, tridymite	respirable	0.05				
	Washington	PEL — Permis- sible Exposure Limit (TWA-8h)	quartz	respirable	0.1	–	no	nd	54
		STEL		respirable	0.3				
		PEL — Permis- sible Exposure Limit (TWA-8h)	cristobalite tridymite	respirable	0.05				
		STEL		respirable	0.15				
40	Poland	NDS — Najwyższe Dopuszczalne Stężenie (TWA-8h) [MAC — Maximum Allow- able Concentration]	dusts with > 50% free (crystalline) silica content	respirable	0.3	0.15–0.3	no	1985	55, 56
				total dust	2	1.0–2.0	no	1959	56, 57
			dusts with 2% to 50% free (crystalline) silica content	respirable	1	0.02–0.5	no	1985	55, 56
				total dust	4	0.08–2.0	no	1976	56, 58

A2; C2 — suspected human carcinogen Ca (NIOSH) — potential occupational carcinogen. K; Cc; group 1; MAK-1 — carcinogenic agent. nd — no data available.

In Japan, OEL-C is interpreted as a maximum recommended value of the concentration measured within 5 minutes (or a shorter period of time). It has been binding since 2006 and is the only standard for respirable crystalline silica dust, except for the limit concerning the concentration of silica dust containing less than 10% of crystalline silica. Apart from Japan, the short-term exposure values have also been adopted by Russia and the state of Washington.

Most of the countries have introduced one standard value for all types of crystalline silica. However, in several countries which defined their standards in 1990s (e.g. Belgium, Chile, Denmark, Estonia, Finland, France, Greece, Spain, Canada, Mexico, Norway, the USA and Sweden) the values for quartz, cristobalite and tridymite have been considered separately. In these countries, the limit concentrations for cristobalite and tridymite are 50% as low as for quartz exposure.

In 2006, ACGIH, while defining the basics and directions of changes in the research-based setting of hygienic standards, decided to adopt the value of 0.025 mg/m³ as the exposure limit for respirable crystalline silica that would protect almost all the exposed workers against lung fibrosis that can be a risk factor of cancer [17]. Moreover, since the results of epidemiological studies did not reveal significant differences between exposure to various polymorphs of crystalline SiO₂ and the development of lung fibrosis, the same standard was adopted also for α -quartz and cristobalite. One year earlier, in 2005, ACGIH had withdrawn the standards for tridymite due to the lack of sufficient data regarding its adverse effects in work environment [59]. NIOSH which has presented a more practical approach to the workers' health protection, in 1974 recommended a limit value of 0.05 mg/m³ for crystalline silica. This value was established taking into account the technical capacity of the equipment used for the collection of air samples, and the detection limits of the analytical methods used for quantitative determinations of silica [4]. In the European Union, the Scientific Committee on Occupational Exposure Limits (SCOEL) has been working for several years on its own lists of indicative

limit values for occupational exposure. In addition to this, appropriate directives of the European Commission make it obligatory for the Member States to define national limit values based on the EU value. However, the lists of hygienic standards published so far, that include about 90 chemical substances, have not contained any standards for crystalline silica [12–14]. The standard values for respirable crystalline silica adopted by most of the countries do not exceed the value of 0.1 mg/m³ (Argentina, Australia, Belgium, Bulgaria, Chile, the Czech Republic, Denmark, Estonia, France, Greece, Spain, India, Ireland, Canada, Mexico, Norway, Portugal, Slovakia, Sweden, the USA, Hungary, Great Britain and Italy). Some countries (Austria, Finland, Luxemburg, New Zealand, Slovenia and Switzerland) have adopted the limit value within the range of 0.15–0.2 mg/m³. Higher values for crystalline silica are binding in Poland, RPA (except for mining and energy industry) and Thailand. The highest concentration limits in Poland refer to dusts containing 2–50% and 50–100% free crystalline silica. For the 100% free crystalline silica, they range from 0.02 to 0.5 mg/m³. The commonly adopted limit value of 0.1 mg/m³ is binding only for exposure to dust containing from 2% to 10% of silica, with the exception of coal dust exposure. The highest MAC values for exposure to industrial dust, of 0.3–0.5 mg/m³, are those referring to dust with free crystalline silica content of 30–50% that can be found in coal mines, quarries, building stone works, ceramic plants and many other worksites.

Lithuania and Russia have not established the standard values for respirable crystalline silica in work environment. However, the limit concentrations for total silica dust in these countries can be used as a basis for estimating the respirable fraction concentrations that can actually be encountered. The data for Poland, regarding exposure to dust containing free crystalline silica, that have been collected for several years, indicate that respirable dust concentrations are usually 4–5 times (less frequently 10 times) as low as the total dust concentrations (unpublished data). Thus, it can be assumed that in Lithuania, the limit value for respirable silica concentration, in



exposure to dust containing 50–70% free crystalline silica, would amount approximately to 0.35 mg/m³. In Russia, the value assessed in the same way would be lower and approximate 0.25 mg/m³.

As for Germany, no standard value has been established for crystalline silica since the chemical has been included in the list of category 1 carcinogens, and it is impossible to define a safety level for such substances. Consequently, no limit values are proposed and the employers are obliged to minimize exposure to such substances in work environment.

Crystalline silica as a human carcinogen

The carcinogenic potential of crystalline silica was already investigated in 1980s. In 1987, the Working Group of the International Agency for Research on Cancer (IARC), having analyzed evidence from animal experiments and the limited evidence for humans that indicated a potential carcinogenic effect of silica, amended the list of probable carcinogens with silica [60]. Ten years later, on the basis of further epidemiological studies (although non-homogeneous), IARC classified two crystalline forms of crystalline silica: quartz and cristobalite, to Group 1 human carcinogens [21]. The decision made by IARC did not eliminate the problem of the carcinogenic effect of silica. A review of recent epidemiological studies conducted in 1996–2005 among workers exposed to crystalline silica clearly indicates a relationship between lung cancer and the occurrence of silicosis. However, it has not been elucidated whether silica may have had a carcinogenic effect on the exposed workers who did not develop the silicosis-like changes in the lung [61].

Apart from IARC, the lists of occupational carcinogens have been developed by prestigious American organizations such as ACGIH, NIOSH, and the National Toxicology Program (NTP), as well as by the European Union and some national organizations including Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area, of the German Research Foundation. The documents published by ACGIH, classified quartz and cristobalite into Group A2, of suspected human carcinogens [18]. NIOSH and NTP considered the three basic

forms of crystalline silica: quartz, cristobalite and tridymite, as occupational carcinogens and human carcinogens, respectively [18]. Likewise, in Germany, these silica forms are classified as category 1 carcinogens, i.e. the substances known to cause cancer in humans or considered to increase the risk of cancer development [18]. The European Union has developed a list of chemical substances known to be carcinogenic to man (category 1); substances which should be regarded as if they are carcinogenic to man (category 2); and substances which cause concern for man owing to possible carcinogenic effects, but in respect of which the available information is not adequate for making a satisfactory assessment (category 3). The list was published in 1967 in Appendix 1 to the Council Directive 67/548/EEC [62]. Since its first publication, the list has been amended several times, including up to 29 Adapting to Technical Progress (ATP) documents [63]. However, crystalline silica was not listed under any of the above-mentioned categories.

The registers of occupational hazards with their respective limit values usually include a note on carcinogenicity. Information about the carcinogenic effect of crystalline silica can be found in the lists of hygienic standards binding in Denmark [30], Netherlands [35], Switzerland [49], Slovakia [46], Norway [44] and Japan [38]. In Argentina [19], Canada, in the provinces of Quebec and British Columbia [25,27], and in New Zealand [43], silica has been claimed to be a probably carcinogenic agent. However, in many countries silica is not classified as a carcinogen; this referring to Austria [21], Belgium [23], France [33], Great Britain [34], Spain [47], Sweden [48], Estonia [31], Bulgaria [24], Australia [20], Chile [28] and the USA — OSHA document [50] and internal regulations of several states [51–54]. In Poland, the Regulation of the Minister of Health and Social Welfare issued in 1996 [64] classified crystalline silica as an agent probably carcinogenic to humans. This Regulation had been in force until 30 March 2005. The new Regulation of the Minister of Health did not include silica among the substances and preparations with a carcinogenic or mutagenic effect under conditions of occupational exposure [65].

FIELD MEASUREMENTS AND THE TESTS CONDUCTED TO COMPARE MEASUREMENT RESULTS WITH OCCUPATIONAL EXPOSURE LIMITS

A substantial part of the assessment of occupational exposure to a given hazard are the measurements and tests used to evaluate whether the hygienic conditions in workplace and exposure level exceed respective standards. These measurements and tests are systematically repeated as a part of the workplace supervision system. In the case of dust exposure including exposure to crystalline silica, the guidelines on the performance of these tests are included in a number of international and European standards that are also binding in Poland. These standards regulate the following issues:

- definitions of terms related to air quality in general and to workplace air quality: PN-ISO 4225:1999 [66] with its Polish supplement PN-ISO 4225/Ak:1999 [67], and PN-EN 1540:2004 [68];
- guidelines on exposure assessment: PN-EN 689:2002 [11];
- characteristics of particle size of fractions for airborne dust measurement: PN-EN 481:1998 [69], PN-ISO 7708:2001 [70];
- technical requirements for equipment used in personal sampling, and evaluation criteria for performance of these instruments: PN-EN 1232:2002 [71], PN-EN 13205:2004 [72];
- general requirements for assessment procedures: PN-EN 482:2002 [73].

The recommendations of the PN-EN 689:2002 standard [11] are general in character and are usually supplemented by guidelines adopted at the national level. In Poland, detailed regulations on the measurements and the tests carried out to compare the measurement results with the limit values, as well as on the calculation of exposure indices and interpretation of results, are included in the PN-Z-04008-7:2002 standard [74]. On the other hand, the mode, methods, and frequency of the measurements and tests are specified in the Regulation of the Minister of Health of 20 April 2005 [75].

As for the assessment of exposure to crystalline silica, the range of the measurements and tests depends on the way the hygienic standard is expressed. In Poland and in other countries in which the limit value for crystalline silica, as a concentration range, has been defined as the maximum concentration level of respirable dust and/or total dust, the exposure indices are average dust concentrations for a standard 8-hour work day/shift. The result of the analysis of free crystalline silica is used solely to select appropriate hygienic standard. Most frequently, when the limit value is given in milligrams of respirable crystalline silica dust in 1 m³ of air, dust concentration is insignificant for the assessment of exposure. What is important is the crystalline silica mass in the air samples.

The collection of air samples and determination of crystalline silica are the necessary steps in exposure assessment, regardless of the way the limit value is expressed.

Air sampling

The principles of air sample collection and concentration measurements of dust particles of different size are usually published as the methods or standards. The methods most commonly used worldwide and approved by the EU Member States for measuring and analyzing dust content in workplace atmosphere [76–78] are as follows:

- MDHS 14/3 [79] developed by HSL, Great Britain,
- NIOSH 0600 [80] and NIOSH 0500 [81] published by NIOSH, USA,
- OSHA PV2121 [82] from OSHA, USA,
- MetroPol Fiche 002 [83] and MetroPol Fiche 085 [84] from INRS, France,
- BIA 6068 [77] and BIA 7284 [78] from Germany,
- MTA/MA-014/A88 [85] from INSHT, Spain.

The methods specified above involve air sample collection by personal sampling in the worker's breathing zone, and gravimetric determination of dust concentration. The differences between these methods refer mainly to the fractions of respirable dust measured and their definitions, as well as the sampling pumps, pre-selectors and filters used, the nominal values of collected air samples and the validation results [77,78]. Most of these methods



concern measurements of respirable dust. However, they do not define the notion of 'respirable dust' in the same way. In the European standard PN-EN 481:1998 [69] and in the international standard PN-ISO 7708:2001 [70], the size distribution of respirable dust is described by a cumulated log-normal distribution, with the median diameter of 4.25 μm and geometric standard deviation of 1.5. The process of collecting air samples to isolate thus defined respirable dust is included in the MDHS 14/3 [79], MTA/MA-014/A88 [85] and MetroPol Fiche 085 [84] methods. Respirable dust, isolated with the use of the OSHA PV2121 [82] and NIOSH 0600 [80] methods, is characterized by a slightly different size distribution of fractions. In the OSHA document [82], the median diameter is shifted towards smaller fractions and equals 3.5 μm , and in the NIOSH publication [80] it equals 4 μm .

The sampling and measurement procedures for the total dust are described in the following methods: MetroPol Fiche 002 [83], MTA/MA-014/A88 [85], NIOSH 0500 [81] and OSHA PV2121 [82]. Other methods, including MDHS 14/3 [79], MetroPol Fiche 085 [84] and BIA 7284 [78] refer to inhalable dust; however, both these terms are considered to be highly similar.

In Poland, the sampling and determination methods for total and respirable dust have been included in two standards: PN-91/Z-04030/06 [86] and PN-91/Z-04030/05 [87]. The procedures of individual dosimetry as described in these standards are generally similar to those pertaining to the European and American methods; however, the operation parameters for the pre-selector (cyclone) refer to only one kind of pre-selector. It is also possible to use other types of selectors, on condition that the air flow rate is adjusted so that the isolated dust fraction would comply with the definition of a respirable fraction as published in the Polish list of concentration limits for dusts. The definition of respirable dust in this document is the same as adopted by OSHA in the USA, i.e. the median diameter of dust particle is 3.5 μm , and the geometric standard deviation 1.5. The basic difference between the methods applied in Poland and those used worldwide is related to the approval of the static sampling. The main disadvantage of the static sampling is the uncertainty whether the collected

samples are equivalent to actual exposure conditions of a given worker.

Methods for determination of crystalline silica

The methods for determining crystalline silica concentrations in workplace have so far been developed mainly in the USA, some European countries and Canada. In the European Union, a database called GESTIS Analytical Methods [76] was created in 2003, which comprises methods for the determination of hazardous substances in workplace. These are the methods used in different European countries and approved by 10 major research institutions in EU. In Poland, the Regulation of the Minister of Health of 20 April 2005 [75] approves the use of the methods that are concordant with the Polish or international standards. As regards workplace exposure to free crystalline silica, the determination methods have been specified in three Polish standards: PN-91/Z-04018/04 [88], PN-91/Z-04018/02 [89] and PN-91/Z-04018/03 [90]. In practice, over 90% of the state laboratories dealing with determinations in work environment use the same method of visible absorption spectrophotometry (a chemical method) according to the PN-91/Z-04018/04 standard [88].

Table 2 presents the methods of analyzing crystalline silica that are included in the GESTIS Analytical Methods database [91,92] and the Polish standardized methods.

The current methods applied to the determination of free crystalline silica in workplace are based on three analytical techniques: X-ray diffraction (XRD), infrared spectrophotometry (FT-IR or IR), and visible absorption spectrophotometry (chemical methods). Two of these methods, namely XRD and IR, make it possible to separately determine the main forms of crystalline silica: quartz, cristobalite and tridymite. The visible absorption spectrophotometry is used to determine the total content of all crystalline forms of silica.

In the determinations, one of the most essential and difficult steps is sample preparation. Only a few of the methods enable direct determination of silica in the samples collected in workplace. The MDHS 101 method [93], ranked first in the GESTIS database [91,92], and the MétroPol Fiche 049 method [94] are the only methods of those presented

Table 2. Methods for determination of crystalline silica approved by the EU for assessment of workplace exposure [91,92] [items 1–10], and Polish standardized methods [items 11–13]

No.	Method	Source — institution, country, year of publication	Sampling procedure, nominal air sample volume	Analytical technique, sample preparation	Reference material	LOD, LOQ, analytical precision (RSD) for quartz
1	MDHS 101 [93]	HSL, Great Britain, 2005	respirable dust collected on PVC (FT-IR) or Ag filter (XRD), according to MDHS 14/3 [79], 0.6 m ³	FT-IR and XRD, sample analyzed directly on filter	quartz SRM 1878 (NIST), Sikron F600 ¹	FT-IR: 3 µg, 0.02 mg/m ³ XRD: 10 µg, 0.05 mg/m ³ FT-IR, XRD: RSD = 0.087
2	MétroPol Fiche 049 [94]	INRS, France, 1999	respirable dust collected on PVC filter, after Fiche 002 [83], 0.6 m ³	XRD, sample < 0.6 mg/cm ² analyzed directly on filter, otherwise demineralized and redeposited onto a polycarbonate filter	no data available	LOQ: 0.05 mg/m ³
3	BIA 8522 [91,92]	Germany, 1995	respirable dust collected on MCE filter, 1 m ³	FT-IR, sample demineralized, preparation in a pellet form with KCl	no data available	LOQ: 0.035 mg/m ³
4	MTA/MA-036 [95]	INSHT, Spain, 2000	respirable dust collected on PVC filter, 0.4 m ³	XRD, sample demineralized and redeposited onto PVC filter	quartz SRM 1878 (NIST), quartz BCR 66 ²	7 µg, 0.06 mg/m ³ RSD = 0.14 range 20–200 µg
5	MTA/MA-057 [96]	INSHT, Spain, 2004	respirable dust collected on PVC filter according to MTA/MA/-014/A88 [85], not defined	FT-IR or IR, sample demineralized, preparation in a pellet form with KBr	quartz SRM 1878 (NIST), quartz BCR 66 ² , quartz SARM 49 ³	no data available
6	NIOSH 7500 [97]	NIOSH, USA, 2003	respirable dust collected on PVC filter, 0.4 m ³	XRD, sample demineralized or dissolved in tetrahydrofuran and redeposited onto Ag filter	quartz SRM 1878 (NIST), cristobalite SRM 1879 (NIST), tridymite ⁴	5 µg, 0.025 mg/m ³ RSD = 0.08 range 50–200 µg
7	NIOSH 7601 [98]	NIOSH, USA, 2003	respirable dust collected on PVC or MCE filter, 0.4 m ³	visible absorption spectrophotometry, sample treated with HNO ₃ , silicate interferences removed in HClO ₄ , crystalline SiO ₂ dissolved in HF and determined as silicomolybdenum blue	quartz SRM 1878 (NIST), cristobalite SRM 1879 (NIST), tridymite ⁴	10 µg, 0.05 mg/m ³ RSD = 0.09
8	NIOSH 7602 [99]	NIOSH, USA, 2003	respirable dust collected on PVC filter, 0.4 m ³	FT-IR or IR, sample demineralized, preparation in a pellet form with KBr	quartz SRM 1878 (NIST), cristobalite SRM 1879 (NIST), tridymite ⁴	5 µg, 0.03 mg/m ³ RSD < 0.15 for 30 µg



Table 2. Methods for determination of crystalline silica approved by the EU for assessment of workplace exposure [91,92] [items 1–10], and Polish standardized methods [items 11–13] — cont.

No.	Method	Source — institution, country, year of publication	Sampling procedure, nominal air sample volume	Analytical technique, sample preparation	Reference material	LOD, LOQ, analytical precision (RSD) for quartz
9	NIOSH 7603 [100]	NIOSH, USA, 2003	respirable coal dust collected on PVC filter, 0.5 m ³	FT-IR or IR, sample demineralized and redeposited onto PVC-acrylonitrile filter	quartz SRM 1878 (NIST)	10 µg, 0.065 mg/m ³ RSD = 0.098 range of 100–500 µg
10	OSHA ID-142 [101]	OSHA, USA, 1996	respirable dust collected on PVC filter, 0.8 m ³	XRD, sample dissolved in tetrahydrofuran and redeposited onto Ag filter	quartz SRM 1878 (NIST), Min-U-Sil 5 ⁵ , cristobalite SRM 1879 (NIST)	5 µg, 0.02 mg/m ³ RSD = 0.11 range of 50–160 µg
11	PN-91/Z-04018/04 [88]	PKNMiJ, Poland 1991	total or respirable dust collected on FiPro ⁶ or PVC filter, according to PN-91/Z-04030/05 [86] or PN-91/Z-04030/06 [87] 0.7 m ³ minimum sample mass — 4 mg	visible absorption spectrophotometry, sample ashed, interferences removed in HCl and HBF ₄ , crystalline SiO ₂ melted with NaHCO ₃ + NaCl, and after dissolving and hydrolyzing the mixture, determined as silicomolibdenum blue	no data available	35 µg, 0.10 mg/m ³ RSD = 0.10 (IOM data for total dust)
12	PN-91/Z-04018/02 [89]	PKNMiJ, Poland 1991	total dust collected on MCE or PVC filter, according to PN-91/Z-04030/05 [86], 0.7 m ³ minimum sample mass — 5 mg	IR, sample demineralized, preparation in a pellet form with KBr	description method of standard quartz preparation	~ 20–25 µg, 0.07 mg/m ³ RSD — no data available
13	PN-91/Z-04018/03 [90]	PKNMiJ, Poland 1991	respirable dust collected on MCE or PVC filter, according to PN-91/Z-04030/06 [87], 0.7 m ³ minimum sample mass — 5 mg	IR, sample demineralized, preparation in a pellet form with KBr	description method of standard quartz preparation	~ 20–25 µg, 0.07 mg/m ³ RSD — no data available

¹ From HSL, Great Britain. ² From IRMM, Belgium. ³ From South Africa Bureau of Standards, SAR. ⁴ From U.S. Geological Survey, USA.

⁵ From Pennsylvania Glass Sand Co., USA. ⁶ Polypropylene microfiber filter.

in Table 2 that do not require any treatment of dust collected on filter before the measurements employing diffraction and infrared spectrophotometry. In other methods, both the samples and the filters are mineralized or dissolved in tetrahydrofuran. Then, the filter deposits are redeposited onto other filters, as in the XRD technique, or they are mixed with potassium bromide or chloride to

yield material to prepare pellets, as in IR spectrophotometry. The methods in the GESTIS database refer to the determination of free crystalline silica in respirable dust. The results of analyses are expressed in such a way that it is possible to directly compare the outcomes with the limit values adopted in most of the EU countries: in milligrams of crystalline silica in 1 m³ of air. The results of analyses

conducted according to Polish standards, expressed as the percentage of silica content, are used only to select appropriate MAC values. Contrary to other analytical methods, this mode requires additional determination of the sample mass. In the determinations of total dust, the use of personal sampling for collecting samples with a required mass during an 8-hour working shift is disputable. It does not apply to the determinations of respirable dust fraction. In work environment, where dust concentrations reach the level of current MAC values [56], to obtain the sample mass recommended for visible absorption spectrophotometry [88], namely of 4 mg respirable dust containing over 50% free crystalline silica, the sample should be collected individually over a period of 12 work shifts. In exposure to dust containing from 2% to 50% free crystalline silica, the sampling would have to last 3 work shifts. Likewise, the estimated sampling time for total dust with crystalline silica content of over 50% would be almost 2 work shifts. Thus, collecting a sample of proper mass during a single 8-h work shift is realistic only in exposure to total dust containing from 2% to 50% free crystalline silica. As it is practically unfeasible to conduct individual sampling during one work day, the method of stationary sample collection has been widely used; however, the results are less representative of the actual conditions of occupational exposure.

In determining free crystalline silica, the dusts isolated from workplace air usually contain many other substances that may have influence on the results of analysis. The dust components in question include feldspars, micas, kaolinite, clay minerals, graphite, large quantities of amorphous silica as well as other silicate and aluminosilicate minerals [93,96,97,99,101–104]. The fact that an analyzed sample contains a mixture of different silica forms is another disadvantage, making it difficult to determine the quantity of each component. The physical properties of these substances are so much alike that they hinder the determination. A variety of means and methods have been applied in different countries to overcome this problem. For instance, the methods based on visible absorption spectrophotometry involve removing these dust components as a part of the analytical procedure [88,98]. In XRD methods, the interference resulting from the overlapping diffraction

peaks can be eliminated by analyzing the lines of less intensity that do not overlap with the lines of the other components of the sample. In IR spectrophotometry, the interference is limited by computerized development of the curves correcting their influence, e.g. by scaled subtraction of interferent spectra and forming higher-order derivative spectra [93,96,99,100,102,106,107]. Irrespective of the method used, it is possible to carry out a procedure of removing some sample components by ashing or chemically dissolving them, prior to the analytical measurements [96,99,102].

All the methods used for the determination of crystalline silica forms in work environment are comparative methods that require calibration with reference materials. The methods worked out by HSL, NIOSH, OSHA and INSHT recommend the use of certified reference materials of the highest quality that derive from NIST, US. These are respirable α -quartz SRM 1878a and respirable cristobalite SRM 1879a. Other recommended reference materials include Sikron F600 (quartz A9950) from HSL, UK, and to a less extent BCR 66 from IRMM, Belgium, as well as the materials used in individual countries, for instance Min-U-Sil 5 in the USA. The Polish methods do not recommend any reference materials; the description of determinations employing infrared spectrophotometry contains a brief outline of preparing in-house standards. Another problem is the lack of certified reference material for analysis of crystalline silica in total dust.

The results of determinations of free crystalline silica, conducted using the same method but calibrated with different quartz standards as the reference materials, can differ significantly. The literature on this subject indicates that some quartz reference materials are characterized by a lower content of crystalline silica (from several to 30%) as compared to quartz SRM 1878a from NIST that is usually used as the basis for comparisons [108–111]. Moreover, the reference materials differ in the distribution of particle size, which can also have influence on calibration results [109,110].

Another source of the differences between determination results can be the way of preparing samples for analysis. In the studies by Kauffer et al. [112], the results obtained



from direct on-filter determinations were several per cent higher than the results from the indirect methods. The authors explain the observed inconsistency in results by the elimination or conversion of some components, including interferences, during sample mineralization, and a higher probability of losing the substance analyzed during some additional analytical procedures. A comparison of the average results of determinations employing the XRD and IR techniques revealed a high consistency. The findings obtained when the XRD method was used were about 2% higher than the results from the IR method [112]. The inter-laboratory comparisons of determination results, such as WASP conducted by HSE, UK [113] and PAT by AIHA, USA [114], as well as the research conducted by Pickard et al. [115] proved that the average values of the results obtained using the XRD and IR methods, differ by several per cent maximally and can be considered comparable.

More substantial differences were noted while examining the influence of dust components on the results of determining free crystalline silica. The results yielded by the IR method were more likely to be affected by interferences than those obtained using the XRD method [114]. Moreover, WASP proficiency testing [113] revealed that the analyses conducted directly on the filters were more precise than the analyses employing an indirect method. The highest differences between the average results were observed in PAT proficiency testing [114], when the comparison concerned determination results from a chemical method congruent with NIOSH 7601 [98] and the IR and XRD methods. The chemical method provided results that differed by about 20% from those obtained via other methods, regardless of the crystalline silica content in the sample. The differences were higher for low silica content (40–60 µg) and decreased in determinations with a substantial silica content exceeding 140 µg.

It is not possible to compare the determination results for crystalline silica as obtained from the methods used in Poland with those used abroad, due to the different fractions of dust analyzed. In Poland, free crystalline silica is determined mainly in total dust, while in other countries in respirable dust. Only one comparison [116] refers to

the results of determination in total dust — the chemical method, congruent with the PN-91/Z-04018/04 standard [88], was compared with the IR method after NIOSH 7602 [99] modified with respect to sample preparation, and with the XRD method (internal standard). The comparisons revealed a high correlation coefficient ($r > 0.99$) between the results obtained from particular methods. However, the differences between the results varied from several % to 30%, depending on the free crystalline silica content and the occurrence of interferences.

The methods for the determination of free crystalline silica in workplace that are recommended by the EU are the validated methods. Table 2 displays the operating parameters for the methods in relation to quartz: limits of detection, limits of quantification (calculated as the concentration of crystalline silica in air volume), and analytical precision. The data indicate that the IR methods are characterized by lower detection and quantification limits. However, evidence from literature implies that the methods have a lower selectivity, compared to XRD methods [4,105,115]. In most of the methods of the GESTIS database, the limits of quantification make it possible to determine crystalline silica at concentrations approaching the currently binding limit values. However, only a few of them: MDHS 101, NIOSH 7500 and OSHA ID-142, can be applied to analyzing free crystalline silica at the safety level defined for work environment. Another important validation parameter, namely the precision of the method, is similar for all the methods and ranges from 8% to 15%. The analysis of results obtained from WASP proficiency testing for within-laboratory variability of determination results showed that the determinations employing the chemical method (congruent with NIOSH 7601 [98]) were significantly less precise [113]. Moreover, the direct methods were characterized by a lower variability of results, compared with the indirect methods.

CONCLUSIONS

The review of the legal regulations and analytical guidelines on the assessment of exposure to free crystalline silica made it possible to draw the following conclusions:

1. It seems advisable to adopt the value of 0.05 mg/m³ as the maximum admissible concentration for respirable crystalline silica dust. The specified MAC value protects the exposed workers from developing silicosis and takes into account the technical capacity of the sampling apparatus and the specific measurement method used for the determinations of free crystalline silica.
2. An improvement of the methods for air sampling and determining crystalline silica concentrations, particularly at low concentration levels, is a major practical problem to be solved.
3. In Poland, the MAC values for crystalline silica, which have been binding unchanged for many years now, need to be verified and adapted to the present exposure conditions. It also seems necessary to implement the determination methods based on analytical techniques: Fourier Transform Infrared Spectrometry (FT-IR) and X-Ray Diffractometry (XRD).

ABBREVIATIONS AND ACRONYMS

- ACGIH — American Conference of Governmental Industrial Hygienists
- AIHA — American Industrial Hygiene Association
- ATP — Adapting to Technical Progress
- FT-IR — Fourier Transform Infrared Spectroscopy
- HSE — Health and Safety Executive, UK
- HSL — Health and Safety Laboratory, UK
- IARC — International Agency for Research on Cancer
- INRS — Institut National de Recherche et de Sécurité, France
- INSHT — Instituto Nacional de Seguridad e Higiene en el Trabajo, Spain
- IR — infrared
- IRMM — Institute for Reference Materials and Measurement
- LOD — limit of detection
- LOQ — limit of quantification
- MCE — mixed cellulose esters
- MDHS — methods for the determination of hazardous substances
- NIOSH — National Institute for Occupational Safety and Health, USA
- NIST — National Institute of Standards and Technology, USA
- NTP — National Toxicology Program, USA
- OSHA — Occupational Safety and Health Administration, USA
- PKNMiJ — Polski Komitet Normalizacji, Miar i Jakości, Poland
- PCV — polyvinyl chloride
- RSD — relative standard deviation
- SMR — standard reference materials
- STEL — short-term exposure limit
- TWA — time-weighted average
- XRD — X-ray diffraction

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