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Hard metals at workplaces: Exposure and evaluation

Abstract

Hard metals are an important material due to their specific properties, such as high degree of hardness and resistance to abrasive wear, and they are in wide use today. There are indications that hard metal aerosols can endanger human health. Discussions are ongoing as to how to categorize hard metals as hazardous as a result. This categorization will require deciding in particular how to determine and evaluate the carcinogenic risks. In order to obtain an overview of this complex subject, this paper explores the presumed health effects on humans, the measurement and analysis procedures, exposure levels at workplaces, and the current state of the art.

1 Introduction

The Senate Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area of the German Research Foundation[1] reported in summer 2004 that based on epidemiological evidence, the inhalable fraction of hard metal aerosols is to be adopted as a carcinogen in humans

(Category 1) [1]:

Hard metal, containing tungsten carbide and cobalt (inhalable fraction)

Addition	Carcinogen category 1 Germ cell mutagen category 3A Additional designation Sah Additional designation H

A position paper with epidemiological justification has been announced but has not yet been published. The Committee on Hazardous Substances (Ausschuss für Gefahrstoffe, AGS) is studying the DFG classification according to EC criteria (Annex VI of the classification Directive 67/548/EEC) with the prospect of incorporating them into the Technical Rule for Hazardous Substances (Technische Regel für Gefahrstoffe, TRGS) 905/906 [2; 3]. This evaluation has not yet been made at this time.

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[1] Senatskommission zur Prüfung gesundheitsschädlicher Arbeitsstoffe der Deutschen Forschungsgemeinschaft (DFG)

The publication has led to uncertainty among the German accident insurers (Unfallversicherungsträger, UVTs) and producers and users of hard metals alike. The questions of how the current state of epidemiological knowledge can be integrated and how a work area must be set up so as to eliminate or keep to an acceptable or tolerable level any risk of causing cancer must be answered. In cooperation with the DFG, the UVTs have begun an interdisciplinary task force with users, producers, scientists and occupational safety professionals which will be actively supporting the evaluation of epidemiological knowledge and will define the state of the art through a comprehensive measuring program.

According to the current principle that the description and categorization of workplaces should take precedence over a limit value, it is the aim of the task force to create BG/BGIA recommendations [4] in which the current procedures and their exposures are described and, if the data are sufficient, to formulate "procedure- and material-specific criteria" according to TRGS 420 [5].

The current state of knowledge and activities is summarized in this article.

2 Production and processing of hard metals

Hard metal is used today for numerous industrial applications. The two major application areas are the wear parts industry and the production of tools for machining metals and other materials. Hard metals include metal alloys that consist mainly of tungsten carbide as the hard material and cobalt as a binding metal. There are also a number of variations with other carbides (e.g., TiC, TaC, NbC, VC) and additional or different binding metals (e.g., Fe, Ni, Cr, Cu).

2.1 Principle of hard metal production

Hard metal production requires essentially the following steps:

- preparation of the powder mixture,
- grinding and mixing,
- granulation, in some cases,
- generation of a green mold,
- machining of the green mold, in some cases,
- sintering of the green mold,
- machining to the finished product.

In the generation and processing of metal powders, process-based dust exposure occurs; it is kept within the lowest possible limits using appropriate ambient air filter systems, local exhaust systems and the use of personal protective equipment (PPE). Through technical progress in recent years, both in exhaust technology and technical systems, workers' exposure has been significantly reduced.

Individual steps in the process, such as filling or maintenance and cleaning of filter systems and machines can cause temporarily higher metal dust concentrations.

2.2 State of the art

The current state of the art for the individual processing steps can be described as follows.

2.2.1 Preparation of the powder mixture

The preparation of the powder mixture is a predominantly manual task, in which the materials are taken from drums in quantities according to the recipe and placed in a grinding and mixing container. Various additives, press aids and possibly solvents are also added to produce a pourable granulate.

In the mixing areas, dust extractors are installed in the room as well as on the mixing containers to prevent dust formation early on. PPE is also worn in this area, such as respiratory protective masks and gloves, in order to prevent skin contact and inhalation of metal dust.

2.2.2 Grinding and mixing

The grinding and mixing are performed in closed containers; worker exposure can only occur when these are being filled and emptied. Dust extraction equipment and PPE are also used during these tasks.

2.2.3 Granulation

For the automatic filling of hydraulic and mechanical presses, a pourable powder granulate is required. This is made from the mixed metal powders using a solvent, e.g., water, acetone, hexane or heptane. The granulate is generated by drying in a closed spray tower in a hot protective gas atmosphere. The finished granulate is removed using airlocks. Worker exposure occurs during filling in batch operation and during continuous removal on the floor of the spray tower before pouring into transport or filling boxes for pressing. Source capture systems and dust protective masks are used here for worker protection.

2.2.4 Generation of a green mold

The finished powder mixtures or granulates are compacted using mechanical or hydraulic presses, by extruding modelling compounds through hydrostatic pressing into what is known as a “green mold”. Worker exposure during this step occurs mainly while filling the mostly automatic press reservoir or when adding the powder mixtures to the hydrostatic press mold parts.

2.2.5 Machining of the green mold

The green mold can be easily machined in order to put it in the desired shape before sintering. A high dust load can arise during mechanical processing of the green mold, requiring high-throughput local extraction in the case of open machines.

The use of modern closed CNC machines considerably reduces dust exposure.

2.2.6 Sintering of the green mold

After the generation of the sintering-ready blanks (the spectrum ranges from cutters for metal processing with low gram-weight to large rollers for the steel industry at over 100 kg) they are sintered in closed sintering furnaces into semi-finished or finished parts. In this step, workers are exposed only during loading and unloading of the furnaces.

2.2.7 Mechanical processing of hard parts

After sintering, the semi-finished parts are brought to their final shape, predominantly by grinding – either dry or using a metal-working fluid (MFW) such as oil, or a special water soluble MWF. Worker exposure during hard machining occurs during the grinding process, especially with dry grinding and with open machines. Closed CNC machines are increasingly being used, helping greatly reduce this exposure. The use of water-soluble MWFs that are specially suited for hard metal processing also helps considerably reduce exposure.

3 Hard metal aerosols at the workplace: evaluation, risks and protective measures

3.1 Terms and risks

The term “hard metal” can be misleading to outsiders. It refers to a sintered mixture of a “hard phase”, the cutting material, and a binding agent, generally cobalt. The composition can vary widely (see section 2).

The discussed risk from inhaling the inhalable dust fraction arises during the entire processing chain, but is very strongly dependent on the condition and the process. First come the production and mixing of the powder, which is followed by the sintering and final shaping by grinding, and then the use as a tool and possible regrinding by the user. The machines and equipment are very different, which leads to very different exposures. These must be quantified as part of a measuring program (see section 7).

3.2 Necessary activities

According to the Occupational Safety Act [6] and the Hazardous Substances Ordinance [7] a risk assessment has to be created and the necessary protective measures to be taken. Current knowledge of the state of the art must therefore be defined for the production and use of hard metal tools.

An evaluation as carcinogenic category 1 or 2 would in principle mean that the extent to which activities and processes can be carried out in closed systems must be investigated. If this is not possible technically, other technical protective measures must be applied and finally PPE used.

4 Epidemiological knowledge

The discussion up to now has primarily considered the epidemiological studies from French hard metal production [8]. Other publications on French hard metal production come from *Lasfargues* et al. (1994) [9] and *Wild* et al. (2000) [10]. There is one epidemiological study out of Sweden as well [11]. In summary, epidemiology does not paint a unified picture in terms of increased risk of illnesses and considering the confounders (other exposures). Furthermore, these studies have hardly any qualitative exposure determinations.

In all studies, aside from the usually occurring exposures to tungsten carbide and cobalt, there were other typical exposures in hard metal workplaces, i.e., the cohorts were defined by the workplace or the activity. It remains unclear what additional exposures there were. An overview analysis of the MEGA database shows that the following other exposures can occur at hard metal workplaces: nickel, iron, chromium, tantalum, niobium, titanium, molybdenum, vanadium, MWFs and solvents, thus predominantly metals. The assured state of knowledge that can be derived from the epidemiology can be summarized as follows:

- Increased risk of illnesses can occur among employees at hard metal workplaces.
- Exposures to tungsten carbide and cobalt occur at hard metal workplaces.
- Exposures to other hazardous materials occur at hard metal workplaces.

It is unclear, however, whether the sometimes observed illnesses among employees at hard metal workplaces are caused by the exposure to tungsten carbide and cobalt, or whether possible health effects that arise can be attributed to other exposures that also occur at hard metal workplaces.

In order to be able to further answer questions for classification and setting limit values, it is necessary to know both the mode of action of the metals in general and the other exposures occurring at hard metal workplaces to evaluate the epidemiological knowledge. In order to determine possible exposures, the measuring program “Exposures at Hard Metal Workplaces” has been run in the BG measurement system for hazardous substances (BGMG) since early 2007 (see section 7).

5 Postulated effect mechanisms of carcinogenic metal compounds

In carcinogenesis by metal compounds, the direct interaction of metal ions with DNA components is of subordinate importance. Nevertheless, for some metal compounds, oxidative DNA damage has been proven in cellular test systems. These are caused by indirect mechanisms, however. Examples include the catalysis of reactions with H_2O_2 through transition metal ions and the generation of very reactive hydroxyl radicals as well as the deactivation of protective enzymes with respect to reactive oxygen species (ROS) (**Figure 1**).

Furthermore, for some metals, changes have been observed in the DNA methylation pattern, which can lead to altered gene expression patterns; in this connection the activation of growth genes (oncogenes) or the deactivation of tumor suppressor genes is especially critical in the context of carcinogenesis. Most results, however, have to do with modulation of DNA repair systems; here, studies in recent years have shown considerable progress regarding the molecular targets.

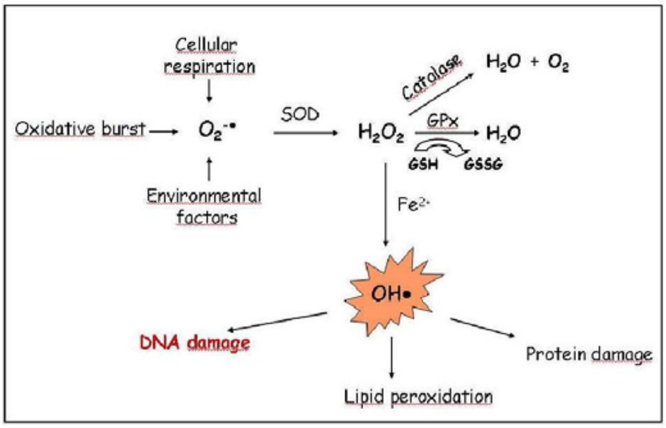

Figure 1:
Cellular response to DNA damage and its influence by carcinogenic metal compounds

The DNA is permanently damaged by endogenic metabolic processes and by a number of environmental factors. The frequency of mutations is on the one hand determined by the damage to the DNA by exogenic and endogenic factors and on the other hand by the cellular response to this DNA damage. The latter encompasses DNA repair processes which are activated depending on the type of damage. In addition, the cell also has other protective and tolerance mechanisms. Thus, DNA damage causes cell cycle arrest at the time of the DNA replication; apoptosis allows the elimination of severely damaged cells from the tissue. Mutations occur largely due to the activation of so-called “error-prone” DNA polymerases, which have the ability to polymerize on the damaged DNA template and thus to convert remaining DNA damage into altered DNA base pairs. Thus, the stability of the DNA depends crucially on the existence of a complex network of DNA repair systems (**Figure 2**).

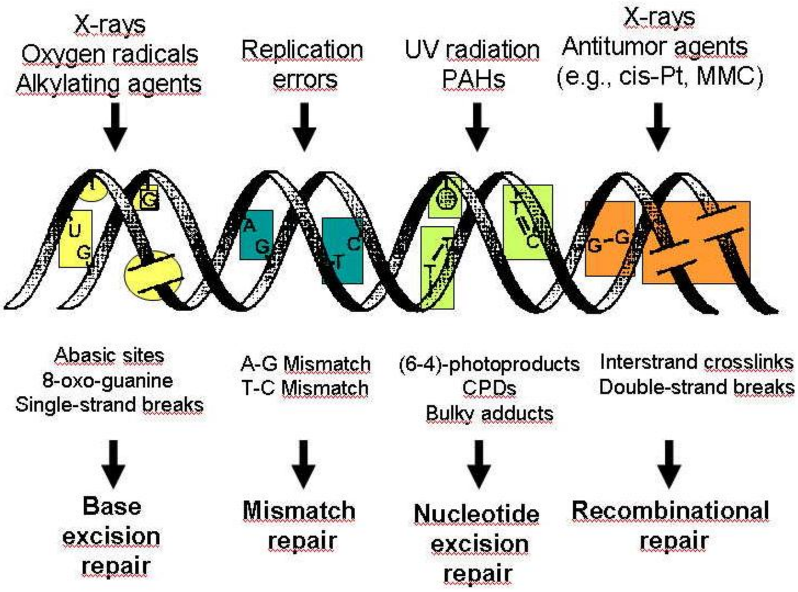

Figure 2:
DNA repair systems

In particular the so-called base excision repair (BER) and the nucleotide excision repair (NER), in which damaged nucleotides are cut out from a strand of DNA and the now missing information can be read out from the other, intact strand again are largely error-free processes. The principal sequence includes damage recognition, the incision at sites of damage and the excision of the damaged DNA segment, the replacement of the excised nucleotides through polymerization and finally the ligation of the newly synthesized DNA segment with the original DNA strand. BER predominantly removes DNA base damage caused by endogenous processes, such as the generation of reactive oxygen species; here the damage is detected by specific enzymes, known as glycosylases. The substrate spectrum of NER is broader by comparison: Here, DNA damage causing more or less pronounced structural changes in the DNA is detected and the introduction of the repair process requires the coordinated interaction of more than 20 proteins.

In recent years, various studies have shown that metal compounds in comparatively low, otherwise not cytotoxic concentrations inhibit various DNA repair processes. Thus, it has been shown that neither nickel nor cadmium induce oxidative DNA base damage in biologically relevant concentrations, but compounds of both metals block the repair of oxidative DNA base damage through BER completely, however. A similar phenomenon applies to nucleotide excision repair: This repair system is impaired in the presence of nickel, cadmium, cobalt and arsenic, with different steps in the repair process being affected. Further experiments then showed that nickel and cadmium compounds not only impede the actual repair process, but the very process of damage detection by repair proteins.

Regarding carcinogenic metal compounds, the inhibition of DNA repair processes is a common mechanism shared by cadmium, cobalt, nickel and arsenic compounds. Nevertheless, the underlying molecular reactions are different and depend in particular on the ability of the specific toxic metal ions to displace essential metal ions from their binding sites and/or to oxidize critical target structures [12].

Nickel has a high toxicity: Both water soluble and particulate nickel compounds are carcinogenic in humans; in animal studies, compounds of intermediate solubility and intermediate toxicity, such as nickel sulfide (NiS) and nickel subsulfide (αNi_3S_2) were among the most severe known carcinogens. Crucial factors are solubility in extracellular fluids, the uptake of the compounds in the cells of the target organs and the subsequent intracellular release of nickel ions as the ultimate damaging agent [13].

The effect of other metals is also the subject of research. It is important that the effect of the different species can be qualitatively the same, the decisive factors for quantitative differences in the DNA damage, however, are the bioavailability and biological half-life [14].

The question arises, why DNA repair systems are such sensitive cellular targets for toxic metal compounds. A possibly important mechanism exists in the competition between toxic and essential metal ions. One aspect that has been pursued for some years in the research is the interaction of toxic metal ions with so-called “zinc finger” structures. “Zinc fingers” refers to various protein motifs where zinc ions complex four specific cysteine and/or histidine residues in order to stabilize the structure of a small, autonomously folded protein domain.

The first zinc finger motifs with this typical folding, which contains one zinc ion, were first discovered in the mid-1980s in transcription factors, which bind to specific DNA sequences and thus introduce the targeted expression of specific genes. Overall, the results today indicate that zinc-binding domains, i.e. defined molecule parts of the protein, can be sensitive target structures for toxic metal ions [15]. However, the tested metals have different effects, and the results also clearly differ depending on the protein studied. Thus, each zinc finger structure has its own characteristic properties and sensitivities to toxic metal ions [16; 17].

The possible relevance of the repair inhibitions for the carcinogenicity of metal compounds becomes clear from the biological significance of the repair systems studied. Thus, the excision repair, in which the damaged DNA segments are removed and replaced is a largely error-free process whose deactivation eliminates an important protective mechanism both with respect to endogenous DNA damage processes and with respect to environmental mutagens. As a result, this leads to increased incidence of mutations and thus to an increased risk of cancer. The underlying molecular mechanisms of the metal effects are the subject of current and future research activities.

6 Analytic determination of hard metal dusts (tungsten carbide and cobalt)

All exposures occurring in the workplace can have effects on health, not just exposure to tungsten carbide and cobalt. According to current knowledge from epidemiology, only statements on hard metal workplaces can thus be made. The following lists of analytical methods, however, relate only to these two substances, since for them compared to other possible exposures the referring measurement analysis and strategies are not so well-developed. Before beginning a measurement program, the existing metal analysis should be tested for its suitability for testing of hard metal exposures. The goal was to develop an analysis method that should be simple, fast and sensitive and delivers a maximum of information on the dust composition. Hard metals are compound materials that consist of a hard phase, often tungsten carbide, and a soft metallic binding phase, often cobalt (about 15 to 20% by volume). Other compositions of carbides and metals are possible, however (**Table 1**).

Table 1:
Hard material phases and binding phases in hard metals

Hard material phase	Binding phase
WC	**Co**
TiC	Ni
TaC	Cr
NbC	Fe
Cr_3C_2	
VC	

The tests were performed with standard reference materials, material samples of known composition and air samples from the region of the hard metal production. They were largely limited to the determination of tungsten and cobalt.

6.1 Digestion method

In the first step, a suitable digestion method must be found. All tests were carried out using the standard reference material SRM 889 from NBS in Gaithersburg, USA; the required analyses were performed using ICP mass spectrometry.

The digestion method [18] suggested by the DFG for testing the MAK values with a mixture of two parts nitric acid (≥ 65 %) and one part hydrochloric acid (25 %) proved well-suited for determining cobalt, while a complete determination of tungsten from tungsten carbide does not succeed. Here, microwave pressure digestion (MWD) proved superior. The MWD applied was optimized in advance regarding the digestion program and acid composition. In addition to the standard reference material SRM 889, other standards and other analysis methods (AAS, ICP-OES) were used. The following conditions have finally been found to be suitable:

- equipment: Mars 5, CEM, Kamp-Lintfort
- acid mixture: 6 parts nitric acid (> 65%), 2 parts hydrochloric acid (35%),
  1 part hydrofluoric acid (40%)
- Acid volumes: 18 ml
- net weight: 40 mg
- temperature: 200 °C
- reaction time: 30 min

6.2 Comparison of analysis methods (material samples)

In addition to ICP-OES and ICP-MS, another analysis method should be used, total reflection X-ray fluorescence (TXRF), since under some conditions the complex sample preparation can be eliminated. With TXRF, many samples can be tested as suspensions, so long as they are stable and are embedded in a matrix provided with internal standards. Material samples are added to an aqueous solution of polyvinyl alcohol, while air dust collected on a cellulose nitrate filter is simply dissolved in acetone (see section 4.3). The latter variant can also be used on material samples when a membrane filter is added dissolved in acetone. TXRF offers additional benefits compared to conventional energy dispersive x-ray fluorescence analysis due to its special radiation geometry, through which the excitation beam is completely reflected on a thin sample film. The secondary radiation is captured above the sample and is hardly influenced by scattered primary radiation. As a result, the spectra indicate only a very low spectral background. Thus, and due to a high fluorescence intensity, low determination limits can be achieved with this method. The following equipment was used for the method comparison:

- ICP-MS: Elan DRC II, PerkinElmer, Rodgau
- ICP-OES: Optima 5300 DV, PerkinElmer, Rodgau
- TXRF: Extra II, Rich. Seifert Röntgenwerk, Ahrensburg

(Seifert no longer sells the unit in this form. Comparable units are sold by Bruker AXS, in Karlsruhe, and CAMECA, in Unterschleißheim).

Ten dust samples from hard metal production in tungsten and cobalt were tested using the above techniques. The samples came largely from extraction units, so that the composition of the dusts were known as far as possible.

In order to permit a comparison between suspension technology and MWD using TXRF, after the analysis of the suspensions, the acetone is vaporized and the residue subjected to MWD. The agreement between ICP-OES and TXRF was particularly good, although only when analyzed using MWD. TXRF analyses after using the suspension technique yielded for tungsten sometimes far too high recoveries (five samples, up to 151%), on the other hand, however, also those that showed good agreement with the other analyses. That spoke for a highly inhomogeneous grain size distribution of the samples and resulting unstable suspensions. In most of the other analyses, the recoveries for both metals were around 100%, independent of the measuring method used. Only one sample showed considerably low findings, for which no plausible explanations could account.

ICP-MS was too sensitive for determining the high tungsten concentrations; in the cobalt analyses there was a good agreement with TXRF.

6.3 Comparison of analysis methods for air samples

Six airborne dusts were studied on cellulose nitrate filters from hard metal production plants. After filter separation, one half was first dissolved in acetone and, displaced with internal standards, tested using TXRF, while the other half was analyzed by MWD using ICP-OES. Next, the acetone was evaporated and the residue subjected to MWD, in order to test it using TXRF this time. Apart from one outlier, all results for both metals showed very good agreement between the different methods. The outlier was presumably the result of an inhomogeneous placement of the filter. For all other cases, the arithmetic mean of the deviations between the measured values for tungsten was 6.6% and for cobalt 4.5%.

6.4 Summary and determination limits

Table 2 shows the determination limits for cobalt and tungsten by analysis method and sample air volume. All methods are suitable for MWD analysis of material samples. Due to its high sensitivity, ICP-MS should only be used to determine very low concentrations.

The suspension method possible for TXRF is unreliable for material samples and should not be used. All methods are suitable for analysis of the metals in airborne dusts. A complex sample preparation can be dispensed with for TXRF since the suspension after filter dissolution with acetone delivers very good results.

For the measuring program described below, therefore, the TXRF method after suspension is preferred due to the simplified sample preparation.

Tabelle 2:
Determination limits of various analysis methods

Metal	Sample removal system	Sample holder type	Air volume in m³	TXRF Susp.	TXRF*	ICP-OES*	ICP-MS*
				in µg/m³			
Co	PAS-pump, GSP-10	MF11301 37 mm	1.2	0.8	1.3	3.4	0.8
W	PAS-pump, GSP-10	MF11301 37 mm	1.2	4.2	4.8	17	1.7
				*method according to MWD			

7 BGMG measuring program for hard metal workplaces

In the BG measurement system for hazardous substances (BGMG), in the context of the evaluation of possible health risks in hard metal workplaces, the measuring program “Exposures at Hard Metal Workplaces” has been carried out since early 2007 in order to systematically determine operating and exposure data as well as measured values in the production and processing of hard metals and to document them in the MEGA exposure database [19] for statistical analysis. The accident insurance associations Berufsgenossenschaft Metall Nord Süd, Maschinenbau- und Metall-Berufsgenossenschaft, Berufsgenossenschaft Elektro Textil Feinmechanik and Berufsgenossenschaft Handel und Warendistribution, together with the BGIA – Institute for Occupational Safety and Health of the German Social Accident Insurance, are participants in the measuring program.

The main focus is on tungsten carbide and cobalt exposure, with exposure to nickel, iron, chromium, tantalum, niobium, titanium, molybdenum and vanadium also determined unless exposure cannot be ruled out.

According to the goals, representative workplace measurements are primarily made using personal BGMG standard methods, as well as stationary measurements when necessary, which allow valid exposure estimates to be made. The respirable (A-dust) and inhalable (E-dust) fractions are also determined. Four samples are taken per work area. The following work areas are of particular interest in the production of hard metals:

- manual weighing of metal powder mixtures,
- pressing,
- shaping the green parts by boring, turning or milling,
- sintering for the final shaping,
- post-processing by dry or wet grinding,
- cleaning the systems.

The focus of the determination for hard metal processing is on dry and wet grinding. **Table 3** shows the measurements available at the end of June 2007, selected by number of measured values.

Of the 252 measured values, 133 are from the production and 119 from the processing of hard metals. The distribution by work area is shown in **Table 4**. This number of measured values does not permit a valid statistical analysis. In the coming months, additional measurements are being taken so that sufficient measurements are available for all work areas for selection and statistical analysis according to the main question.

Table 3:
Number of hazardous substance measurements in hard metal workplace

Hazardous substance	Number
Inhalable fraction	39
Respirable fraction	38
Tungsten and its compounds	38
Cobalt and its compounds	38
Chromium (total chromium)	18
Nickel and its compounds	17
Vanadium and its compounds	10
Metal-working fluids	8
Metal-working fluids, aerosol	8
Titanium and its compounds	8
Tantalum and its compounds	8
Hydrocarbon mixtures, additive-free	8
Niobium and its compounds	6
Molybdenum and its compounds	4
Iron and its compounds	4
Total number of analyses	252

Table 4:
Number of measurements in the production and processing of hard metals

Production of hard metals	
Work area	**Number**
Manual weighing	12
Pressing, general	12
Milling, general	12
Reaction container, general	12
Wet grinding	58
Dry grinding	17
Laser beam cutting	10
Total number of analyses	133
Processing of hard metals	
Work area	**Number**
Wet grinding	87
Dry grinding	32
Total number of analyses	119

8 Outlook

The current state of the art in hard metal production is not comparable with that of 15 years ago. The use of modern closed equipment has greatly reduced worker exposure today. For the future, it is expected that the trend towards closed, further automated equipment will continue and will lead to even further reduced worker exposure.

There is still some processing on open machines, however, where despite more efficient extraction technology, there is certainly still room to reduce exposure. However, it cannot be determined with certainty whether in such cases as a result of the risk evaluation a technical upgrade is necessary or secondary protective measures would be fully sufficient: For the purposes of the "Gefahrstoffverordnung" (Hazardous Substances Ordinance), it is the risk that must be minimized, not the exposure.

The measuring program to determine the typical exposure in hard metal workplaces ends in early 2008. The measured values including the exposure data from the BGMG measuring program are now available for statistical analysis and comprehensive exposure descriptions and thus allow differentiation and quantification of the exposures according to industry, for example. Based on this, the evidence from the epidemiological study results is studied with reference to the evaluation of tungsten carbide and cobalt and BG/BGIA recommendations compiled for the risk evaluation according to the "Gefahrstoffverordnung" for exposure in hard metal workplaces.

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