

Quality improvement and quality testing for the determination of carbon disulphide at workplaces

Th. Göen, P. Kredel, N. Lichtenstein, G. Ruppert, D. Stevenz, U. Stöcker

1 Introduction

Carbon disulphide (CS₂) is a solvent which, due to its high toxic potential, is only used in larger amounts in the viscose industry. During the transformation of cellulose to liquid viscose it is used not as a solvent but as a reagent and can thus at present not be replaced by other, less toxic compounds.

Due to the high toxicity of CS₂, its effects have been the subject of many clinical studies [1]. In almost all of the studies the weak point for the epidemiology was the exposure assessment. Several research groups stated that the analysis of CS₂ in the workplace air does not produce representative results for the individual worker if the samples are collected with stationary sampling systems. They pointed out that the CS₂ concentrations in the air can be highly inhomogeneous and, at some workplaces, can fluctuate widely [1 to 3]. Furthermore, the German Advisory Committee on Existing Chemicals of Environmental Relevance (GDCh-Beratergremium für Altstoffe – BUA) has pointed out to the fact that in most of the investigations the methods of exposure measurements have been badly described and many sources of error are recognizable, generally leading to an underestimation of the exposure to CS₂ [4]. This statement was supported by a study of Göen et al. [5] about several methods using charcoal tubes for sampling of carbon disulphide. They found systematic errors which would have resulted in highly underestimated exposure data if they were unknown or ignored.

Because of the high importance of the quality of exposure assessment for a valid estimation of health based exposure limits, the German Committee of Hazardous Substances (Ausschuss für Gefahrstoffe – AGS) ordered the review, improvement and supplement of the methods for the determination of carbon disulphide in the air. The essential activities were organised and performed by a special working group, which consisted of representatives of the institution for statutory accident insurance and prevention in the chemical industry, the BG Institute for occupational safety (BIA), the industrial hygiene departments of the German and Austrian chemical fibres industry and scientific experts. The tasks of this concerted action were the improvement of existing analytical methods, the development of new methods and the testing of comparability and assurance of new and established methods.

Dr. rer. nat. *Thomas Göen*,
Institut für Arbeitsmedizin des Universitätsklinikums der RWTH Aachen.
Dr.-Ing. *Peter Kredel*,
Berufsgenossenschaft der chemischen Industrie, Köln.
Dr. rer. nat. *Norbert Lichtenstein*,
Berufsgenossenschaftliches Institut für Arbeitssicherheit – BIA, Sankt Augustin.
Dr. rer. nat. *Gerda Ruppert*,
Acordis Analytical Services, Obernburg.
Dr. rer. nat. *Dieter Stevenz*,
Analytisches Labor der BG Chemie, Leuna.
Dr. rer. nat. *Ulrich Stöcker*,
Acordis, Wuppertal.

Abstract The review and re-fixing of an exposure limit value for carbon disulphide (CS₂) faced problems, because several methods used in the past for the determination of carbon disulphide in the air gave only low reliabilities and systematic errors. The aim of a concerted action of the institution for statutory accident insurance and prevention in the chemical industry, the BG Institute for occupational safety – BIA, the German and Austrian viscose industry and scientific experts was the improvement of the CS₂ analysis in the air. One of the activities was the improvement of the desorption process of carbon disulphide from activated charcoal. The improved sample preparation was combined especially with high resolution gas-chromatography (GC) and mass spectrometry. Furthermore new methods were developed and validated for personal sampling of CS₂. Several methods were compared in a proficiency test under real conditions. This led to higher reliabilities and a high comparability of the methods which use GC-procedures. It was shown that the reliabilities of photometric techniques were too low for the assessment of current exposure limits.

Qualitätsverbesserung und Qualitätsprüfung für die Bestimmung von Schwefelkohlenstoff am Arbeitsplatz

Zusammenfassung Die Überprüfung und Neu-Festsetzung eines Grenzwertes für Schwefelkohlenstoff (CS₂) ist problematisch, weil in der Vergangenheit vielfach Verfahren zur Bestimmung von Schwefelkohlenstoff in der Arbeitsplatzluft verwendet wurden, die geringe Zuverlässigkeitskriterien und systematische Fehler aufwiesen. Deshalb wurde von der Berufsgenossenschaft der chemischen Industrie, dem Berufsgenossenschaftlichen Institut für Arbeitssicherheit – BIA, der Viskose-Industrie und wissenschaftlichen Experten eine konzertierte Aktion zur Verbesserung der CS₂-Analytik initiiert. Eine der Maßnahmen bestand in der Verbesserung der CS₂-Desorption von Aktivkohle. Die verbesserte Probenaufarbeitung wurde vornehmlich mit der Kapillar-Gaschromatografie/Massenspektrometrie gekoppelt. Darüber hinaus wurden neue Verfahren für die personengebundene Probenahme entwickelt und optimiert. Die Methoden wurden in einem Ringversuch unter Realbedingungen verglichen. Die Ergebnisse zeigten verbesserte Zuverlässigkeitskriterien und eine hohe Vergleichbarkeit der GC-Methoden. Die Zuverlässigkeit von photometrischen Verfahren erwies sich als zu gering, um vorliegende CS₂-Belastungen zu überwachen.

2 Existing methods and insufficiencies

For the determination of carbon disulphide in the air several different techniques and methods are available [4]. The direct determination of carbon disulphide in the air is done by infrared spectrometry and gas-chromatography (GC). Low concentrations of CS₂ are analysed by gas-chromatography after concentration in cryogenic or adsorption traps. After gas-chromatographic separation, CS₂ is recorded by photo-ionisation detection or flame-photometric detection. More common is the splitting of sampling (at the workplace) and analytical determination (in the laboratory). The sampling of

carbon disulphide can be done in gas-collection tubes or Tedlar bags, in absorption solution and on adsorption tubes. However, the sampling in gas-collection tubes and absorption solutions have disadvantages for personal sampling. Because of its high specific surface and the well-balancing adsorption enthalpy of CS₂, activated charcoal is the most frequently used adsorption material for the air sampling of carbon disulphide [5]. The accumulation of carbon disulphide in adsorption tubes is performed by suction pumps (active sampling) and by diffusive sampling (passive sampling), respectively. Solvents or *Viles* reagent (Cu acetate/diethylamine/triethanolamine/ethanol) are used for the desorption of CS₂ from activated charcoal. The photometric analysis of the *Viles* reaction product (copper diethyldithiocarbamate) is one of the oldest techniques to determine carbon disulphide [6]. Because of the low sensitivity of the photometric detection the use of this technique has decreased in the last years. Gas-chromatographic methods for the analysis of carbon disulphide have been developed since the 1970s using flame photometric (FPD), photo-ionisation, and electron-capture (ECD) detectors. These methods have been used frequently in toxicological studies and for the measurement of workplace exposure during the last ten years [7]. In general, the gas-chromatographic techniques show very well acceptable values of sensitivity and selectivity for the determination of carbon disulphide.

The weak point of the methods using charcoal adsorption tubes is the desorption process. Losses of CS₂ at this step of the procedure can cause highly underestimated results. The desorption efficiency depends on the amount of the adsorptive [8], the quotient of eluate volume and charcoal amount [5], and the solvent used for desorption. Using active sampling tubes and 10 ml toluene for desorption of CS₂, desorption efficiencies less than 75 % were found for low amounts of carbon disulphide in the tubes [8]. An extremely low efficiency of 45 % was found for the desorption of carbon disulphide from ORSA tubes caused by the high amount of charcoal of this diffusive sampler [5]. The problem of systematic errors caused by a low desorption efficiency can be solved when users of this method will determine the recovery rates by themselves and use these rates for data correction. However, procedures with low desorption efficiency are susceptible to accidental errors and to the dependence on other influence factors (e. g. amount of CS₂ adsorbed).

3 Activities of the concerted action for quality improvement and assessment

3.1 Improvement of existing methods

The efficiency of the desorption process can be improved by the choice of the desorption solvent and by an enlargement of the solvent amount. The latter has the disadvantage of increasing the dilution factor and thus the detection limit. Therefore an enlargement of the solvent amount cannot be recommended generally for the improvement of existing methods for the determination of carbon disulphide in the air.

Nevertheless in special cases, the decrease of sensitivity can be compensated by high sampling volume and a sensitive detection system. The industrial hygiene laboratory of Acordis Kelheim developed a method using 20 ml toluene

(Dräger type NIOSH) and 50 ml toluene (Dräger type B), respectively, for desorption and a GC-FPD (flame-photometric detector) system for CS₂ detection. For both sampling systems, a quantitative desorption of the adsorbed carbon disulphide was demonstrated [9; 10].

The analytical laboratory of the institution for statutory accident insurance and prevention in the chemical industry in Leuna improved their method for the determination of carbon disulphide by changing the desorption solvent. In the new method 10 ml of a mixture of toluene and dichloromethane (9/1 v/v) is used for the desorption instead of the same volume of pure toluene. The desorption efficiency was determined to be 80 % [11]. In this method, electron-capture detector (ECD) and mass-spectrometry can be used for the detection of carbon disulphide. The use of an ECD has the disadvantage that it has to be coupled with an excellent gas-chromatographic separation because of the dominant peak of dichloromethane in the chromatogram.

The laboratory of the department of occupational medicine of the university of Aachen improved their method to determine carbon disulphide in the air by passive sampling in the same way as the laboratory in Leuna. For the desorption of carbon disulphide from the charcoal layer of the ORSA monitor (400 mg charcoal) 10 ml of a mixture of toluene and dichloromethane (9/1 v/v) are used. Because of the problems of electron-capture detection, a pulsed flame-photometric detector is used as an alternative to the mass-spectrometric detection. For the desorption process efficiency rates of 78 to 79 % were found [12].

3.2 New methods

An alternative to the desorption of volatile substances from adsorption materials is the application of the thermodesorption technique. The advantage of this technique is a shorter preparation of the sample by direct inlet of the desorbed substance into the GC system. Furthermore the method is more automated and prepared for a high number of samples. Acordis Analytical Services developed a new procedure using Carboxen-569 as an adsorption material, a thermodesorption injector and a GC-MS system for the determination of CS₂ in air samples of the viscose industry. The method was validated for active sampling as well as for passive sampling. The calibration of the procedure is performed by CS₂ spiked test gas atmospheres [11; 13].

3.3 Proficiency tests

To compare the various established, improved and new methods performed by different industrial laboratories an intercomparison study was carried out under actual manufacturing conditions in February 2000. Carbon disulphide samples were collected from the air at three different departments of a viscose rayon plant using the different sampling procedures of the participants. In two department sites sampling took place at real conditions; in one department the CS₂ concentration was artificially raised. Charcoal tubes of Dräger type NIOSH, type B and ORSA and thermodesorption tubes with Carboxen 569 and Carbosieve S III were used for sampling. The CS₂ was desorbed from charcoal tubes by toluene, toluene/CH₂Cl₂, ethanol and *Viles* reagent. Fourteen procedures used GC systems, whereas two procedures were carried out with *Viles* reaction and photometric detection. Comparing the results of various sampling procedures no significant

differences were observed in general for those methods with gas-chromatographic analysis. This can also be stated for the comparison between passive and active sampling if for both cases GC systems have been used for analysis. For all sites, a distinct deviation of the results determined by photometric detection from those determined by GC detection was found by differences of means and data variances [7].

In June 2000 a second intercomparison was performed to determine the accuracy of some of the methods. For this, charcoal tubes and thermodesorption tubes were spiked with carbon disulphide using test gas atmospheres. The spiking process was performed in the Institute of Ecological Chemistry of the National Research Center for Environment and Health (GSF – Forschungszentrum für Umwelt und Gesundheit) using a certified test gas generator. The results of the intercomparison show an acceptable accuracy for both, the improved charcoal methods and the thermodesorption procedures [14].

4 Conclusions

The activities of the concerted action of the viscose industry, the institution for statutory accident insurance and prevention and scientific experts lead to an improvement of analytical methods for the determination of carbon disulphide at workplaces. Furthermore new efficient procedures are now available using the thermodesorption technique. It has to be emphasised that the improvements and developments were mainly focused on methods for personal sampling. This is important because personal sampling is the only measurement strategy which allows for a correct assessment of the exposure of the employees in the chemical fibres industry. This point was also stated at a symposium on the consequences of the law on protection against dangerous substances (Gefahrstoffverordnung) in the viscose industry [15; 16].

Because of the information resulting from method validations and intercomparison studies the use of activated charcoal samplers in combination with toluene/CH₂Cl₂ desorption and detection by GC-FPD and GC-MS, respectively, as well as the use of thermodesorption in combination with GC-MS is recommended for the assessment of carbon disulphide without limitations (Table). For this, active and passive sampling can be performed. The use of toluene for the desorption process has not resulted in deviations in the intercomparison study. However, it cannot be recommended without any limitation because of lower desorption efficiencies. The use of GC-ECD in combination with toluene/CH₂Cl₂ can neither be recommended without limitation because of the demands on the chromatographic performance. Definitely not recommendable for the assessment of current exposures to CS₂ is the use of GC-FID and photometric detection (Viles reaction) because of the low sensitivity (GC-FID) and low sensitivity and selectivity (photometric detection), respectively.

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Recommendations for the use of new and established methods for the determination of CS₂ in workplace air.

Sampling procedure	Desorption technique	Detection technique	Remarks
AC, active	toluene	GC-ECD, -FPD, -MS	recommended (with limitations)
AC, active	toluene or toluene/CH ₂ Cl ₂	GC-FID	not recommended
AC, active	toluene/CH ₂ Cl ₂	GC-ECD	recommended (with limitations)
AC, active	toluene/CH ₂ Cl ₂	GC-FPD, -MS	recommended
AC, passive	toluene/CH ₂ Cl ₂	GC-(P)FPD, -MS	recommended
TD, active	thermodesorption	GC-MS	recommended
TD, passive	thermodesorption	GC-MS	recommended
AC, passive	ethanol or Viles-reagent	Viles reaction and photometric detection	not recommended

AC = activated charcoal

TD = Carboxen 569

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