Chemical Hazards in the Workplace

Measurement and Control

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National Institute for Occupational Safety and Health

Based on a symposium
sponsored by the Division of
Chemical Health and Safety at the
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Chemical Hazards in the Workplace

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M. Joan Comstock, *Series Editor*

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FOREWORD

The ACS SYMPOSIUM SERIES was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the Series parallels that of the continuing ADVANCES IN CHEMISTRY SERIES except that in order to save time the papers are not typeset but are reproduced as they are submitted by the authors in camera-ready form. Papers are reviewed under the supervision of the Editors with the assistance of the Series Advisory Board and are selected to maintain the integrity of the symposia; however, verbatim reproductions of previously published papers are not accepted. Both reviews and reports of research are acceptable since symposia may embrace both types of presentation.

PREFACE

The workplace environment is a significant part of the total ecological system. Since it can be measured, some control over it can be achieved, and improvements in the control technologies in the workplace can be made. Because of the rapidly growing production of complex chemical substances and the use of these in modern living during the past three decades, the existence of chemical hazards in workplaces in relation to worker health and safety has become the subject of great concern.

Although the industrial hygiene considerations and the federal government involvement in worker health and safety in the United States began a long time ago, concerted effort and increased attention toward this work-related problem—either by government or by industry—did not become possible until about ten years ago when two sister agencies of the government were created, namely, the Occupational Safety and Health Administration (OSHA), which is part of the Department of Labor, and the National Institute for Occupational Safety and Health (NIOSH), which is part of the Department of Health and Human Services. The functions of these agencies are to clean up the workplace environment and to protect workers' health through worker and industry participation, recognition of potential hazards, and conduction of on-site evaluations. The fulfillment of these responsibilities requires the development of new measurement and control methods as well as improving the existing technology.

To achieve meaningful health hazard evaluations and control technologies for the workplace environment, knowledge of correct measurement and monitoring techniques is necessary. The increased number and complexity of chemical species in workplaces has made the occupational environment intricate in nature. Careful measurements are required for any meaningful controls. Therefore, analytical chemists and industrial hygienists working in the occupational health field face a great challenge in measuring and evaluating the workplace environment. New problems are encountered and solutions are sought on a continuing basis. For instance, the work atmosphere could contain various gases and vapors, aerosols, particulates, vapor–particulate mixtures at various temperatures, humidities, and concentrations to which workers may be exposed. Sampling and analytical methods for the substances must be available before any measurement and control efforts are made to meet their health and

safety threatening challenges. In addition, quality control and compliance statistics must be maintained for any meaningful efforts in this regard.

The symposium upon which this book is based was designed to present a current perspective on the measurement and control of chemical hazards in the workplace and to encourage an exchange of ideas among specialists in related areas. This symposium presented both the state-of-the-art and future directions of monitoring and measurement procedures for the occupational environment. Specific topics included: new analytical techniques and methods development; occupational environmental monitoring and control technology (including medical monitoring and analysis); and quality assurance and requirements of compliance statistics.

The authors represent an excellent cross section of the current knowledge in the field of the measurement and control of the occupational environment. The chapters are organized into sections (based on the logical categorization developed for the symposium) on methodology, monitoring and control, special toxicants, quality assurance, and new technologies. I hope that this book will be a source of useful information to those working in the field, and also a valuable contribution to the literature.

I wish to acknowledge, with sincere appreciation, the contributions of the authors and reviewers; without their time-consuming efforts this work would not have been possible. I would also like to thank the ACS Division of Chemical Health and Safety for inviting me to organize the symposium, and the National Institute for Occupational Safety and Health for supporting my participation in this activity.

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October 2, 1980

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Sampling and Analytical Methodology for Workplace Chemical Hazards

State of the Art and Future Trends

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Industrial hygiene sampling and analysis is a rapidly expanding activity in government and industry. Exposures of individuals to toxic substances in workplace environments requires accurate sampling and measurement of gases, liquids and solids. Acceptable methods are now available for at least 400 substances as a result of the NIOSH Standards Completion Program. Miniature impingers and bubblers have been long used for workplace sampling. They are inconvenient to use. Solid sorbent tubes are easier to use and are finding wide applicability.

The conversion to solid sorption media from liquid absorption solutions for collection of gases and vapors is a continuing process. The solid sorbent sampling tube is a small device, easily manipulated, and not prone to lose its contents when being used under awkward sampling conditions or during shipping. These physical factors can improve the accuracy of the final result.

Filter collection media have become available in a wide variety of materials including glass fibers and many synthetic plastic films. This allows for selection of a filter that is compatible with the analytical method in addition to not altering the physical and chemical characteristics of the particles collected. The field of aerosol technology has grown significantly and with the increased knowledge of particle characterization methodology the effects of specific ranges of particulate matter can be analyzed.

Analytical techniques have gone through considerable changes in the past 20 years. With the development of more sensitive and selective analytical instrumentation the analyst has been able to detect and identify minute quantities of materials never before seen. This has brought about a keen awareness of the widespread distribution of toxic hazards and also the need to study the long term effects of low level exposures. The development of new methodology is a dynamic process. However, new methods should always be thoroughly tested to demonstrate the precision and accuracy of the results obtained.

SRI International and Arthur D. Little, Inc. carried out an extensive development and validation study between 1974 and 1979

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for NIOSH in which approximately 400 methods were studied. (1,2) The study was carried out in two phases. In the first phase the major emphasis was on laboratory validation of existing methods. In the second phase more emphasis was placed on methods development and the substances that were studied were selected from those for which validation methods were not available from the first phase. The results of these studies were presented as individual reports for each substance. They are a sampling and analytical method (SAM), a sampling data sheet (SDS), and a backup data report (BUD). The reports on methods have been published by NIOSH and are available through the U.S. Government Printing Office, Washington, D.C.

Protocol for Methods Validation

A detailed protocol for laboratory validation of sampling and analytical methods for toxic substances in workplace environments is given in Figure 1. The literature was searched and a method of sampling and analysis was selected. The next step was to evaluate and, if necessary, develop an analytical method that was compatible with the sampling medium. If a satisfactory analytical method became available only then did we undertake generation of a test atmosphere. Then samples were collected with the appropriate collection medium. Both capacity and collection efficiency were evaluated.

For each method 18 samples were collected and analyzed--6 samples at each of the 1/2, 1, and 2 times the OSHA Standard level. If the results to this point indicated a successful method, then storage stability was evaluated. If all requirements of the protocol were met, the method was considered laboratory-validated and appropriate reports were prepared. At various stages of the protocol, we evaluated the probability of success within the budget for each method. If at any time it became apparent that the method study could not be successfully completed within budget, laboratory work was discontinued and a failure report was prepared.

The basic criterion for successful validation was that a method should come within 25% of the "true value" at the 95% confidence level. To meet this criterion, the protocol for experimental testing and method validation was established with a firm statistical basis. A statistical protocol provided methods of data analysis that allowed the accuracy criterion to be evaluated with statistical parameters estimated from the laboratory test data. It also gave a means to evaluate precision and bias, independently and in combination, to determine the accuracy of sampling and analytical methods. The substances studied in the second phase of the study are summarized in Table I.

Selection of Methods of Sampling and Analysis

A literature search was usually the first step that resulted in the selection of an analytical method consistent with one of the common sampling methods. The objective of these methods is to

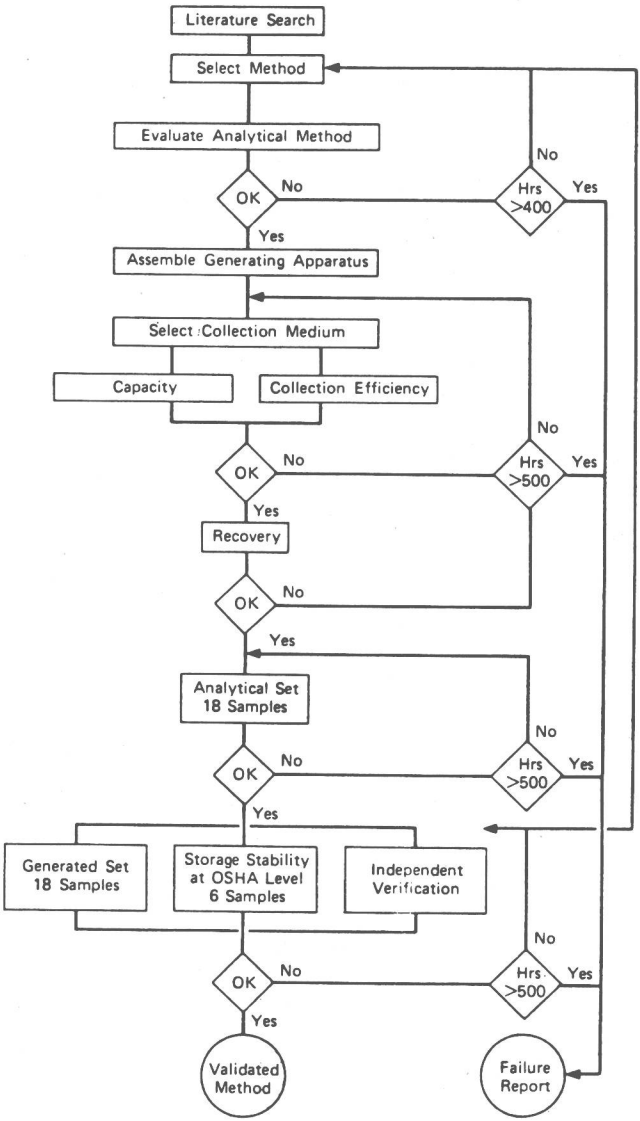

Figure 1. Protocol for method development and validation

Table I Validated Methods

Code	Compound No.	Analyte	OSHA standard (mg/cu m)	Collection medium	Sample treatment *	Analytical method	Range (mg/cu m)
S	S345	Acetaldehyde	360	Bubbler (Girard T)	-	HPLC	170-670
S	S169	Acetic acid	25	Charcoal	Formic acid	GC/FID	12.5-50
S	S342	Alkyl mercury compounds	0.01 (TWA) 0.04 (C)	Carbosieve B	Thermal desorption	Flameless AA	.004-.017 (TWA) .02-.08 (C)
A	S346	Allyl glycidyl ether	45	Tenax GC	Diethyl ether	GC/FID	19-87
S	S158	2-Aminopyridine	2	Tenax GC	Thermal desorption	GC/FID	0.91-3.60
S	S347	Ammonia	35	H_2SO_4 treated silica gel	0.1 N H_2SO_4	ISE	17-68
A	S348	Ammonium sulfamate	15	MCEF	Water	IC/ECond	6.4-27.3
S	S163	Anisidine (ortho & para isomers)	0.5	XAD-2	Methanol	HPLC	0.25-1.16
A	S2	Antimony & compounds	0.5	MCEF	HCl	AA	0.258-1.08
S	S276	ANTU	0.3	PTFE filter	Methanol	HPLC	0.128-0.76
S	S253	Benzoyl peroxide	5	MCEF	Diethyl ether	HPLC	3.12-19.10
A	S138	n-Butylamine	15 (C)	H_2SO_4 treated silica gel	50% aq. methanol	GC/FID	8.1-35.5
S	S350	n-Butyl mercaptan	35	Chromosorb 104	Acetone	GC/FPD-S	16.8-74
A	S313	Cadmium fume	0.1 (TWA) 0.3 (C)	MCEF	HNO_3/HCl	AA	0.04-0.175 (TWA) 0.122-0.57 (C)
A	S249	Carbon dioxide	5000 ppm	Bag	-	GC/TCD	2270-10,000 ppm
A	S340	Carbon monoxide	50 ppm	Bag	-	Electrochemical	24.7-115.4 ppm
A	S278	Chlordane	0.5	MCEF/Chromosorb 102	Toluene	GC/ECD	0.156-1.17
S	S11	Chloroacetaldehyde	3 (C)	Silica gel	50% aq. methanol	GC/ECD	1.8-6.4
S	S120	Chlorodiphenyl, 42% Cl	1	Glass fiber filter/ Bubbler (isooctane)	Isooctane	GC/ECond	0.51-2.7
A	S211	1-Chloro-1-nitropropane	100	Chromosorb 108	Ethyl acetate	GC/FID	51-206
S	S112	Chloroprene	90	Charcoal	Carbon disulfide	GC/FID	44-174
A	S203	Cobalt metal fume & dust	0.1	MCEF	Aqua regia	AA	0.031-0.22 (f) 0.040-0.26 (d)
S	S354	Copper fume	0.1	MCEF	HNO_3	AA	0.05-0.37
S	S356	Crag herbicide	15	MCEF	Water/methylene blue complex	Colori.	5-27
S	S279	2,4-D	10	Glass fiber filter	Methanol	HPLC	5.1-20.3
S	S280	Demeton	0.1	MCEF/XAD-2	Toluene	GC/FPD-P	0.06-0.33
S	S111	Dichlorodifluoromethane	4950	Charcoal	Methylene chloride	GC/FID	2940-10,500
A	S109	Dichloromonofluoromethane	4200	Charcoal	Carbon disulfide	GC/FID	1730-7600
S	S108	Dichlorotetrafluoroethane	7000	Charcoal	Methylene chloride	GC/FID	3500-14,100
S	S140	Diethylaminoethanol	50	Silica gel	Acidify with HCl, desorb w/MeOH-H_2O basify w/NaOH-MeOH	GC/FID	25-113