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BEIJING SPECIALITY GAS RESEARCH & DEVELOPMENT CENTRE

DP/CPR/85/005/11-03

CHINA

Conclusive Technical Report: Atomic Absorption Spectrography Analysis\*

Prepared for the Government of the People's Republic of China  
by the United Nations Industrial Development Organization,  
acting as executing agency for the United Nations Development Programme

Based on the work of Juraj Bercik  
Expert in Atomic Absorption Spectrography Analysis

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United Nations Industrial Development Organization  
Vienna

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Explanatory notes

Value of the local currency during the period of the mission :

US \$ 1.00 = 3.70 Yuan Renmi /RMB/

RMB Yuan 1.00 = 0.27 US \$

Some technical abbreviations :

- BSGRI - Beijing Specialty Gas Research Institute
- AAS - Atomic Absorption Spectrophotometry
- FAAS - Flame Atomic Absorption Spectrophotometry
- GFAAS - Graphite Furnace Atomic Absorption Spectrophotometry
- MHS - Mercury Hydride System
- EDTA - Ethylenediaminetetraacetic acid
- DL - Detection Limit
- VLSI - Very Large Scale Integration
- OES - Optical Emission Spectroscopy
- ICP - Inductive Coupled Plasma
- DPP - Differential Pulse Polarography
- ESA - Electrochemical Stripping Analysis

Abstract

Project: Beijing Specialty Gases Research and Developing  
Centers, Atomic Absorption Spectrography Analysis  
DP/CPR/85/005/11-03/

Government Implementing Agency : Bureau of Chemical Industry  
of Beijing Municipal Government

Executing Agency : UNIDO

Name of expert : Juraj Berčík

Duty Station : Beijing, BSGRI, Dajiaoting, Chaoyang District,  
Peoples Republik of China

Duration : 16 days, August 1987

Expert was fielded on the project for the branch of Atomic Absorption Spectrophotometry. His main duty and task was to develop the capabilities of BSGRI personnel to set up, operate and utilize the atomic absorption spectrophotometry apparatus for ultratrace metal analysis /ppb levels/ in electronic grade high purity gases and dopant materials used for semiconductor manufacturing. Some sampling systems for separation, collection and enrichment of gas-borne particles were proposed.

Lectures about AAS, Selection and optimisation of AAS, Operating conditions, Advanced analytical methods for trace analysis, Sampling and collecting of gas-borne particles, Problems in ultratrace analysis and Advanced analytical instrument in gas analysis were made.

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## Introduction

The essential needs for chemical raw materials in ultrahigh purity states have been well established in the electronics industry. Exceptionally pure gases and volatile reagents have become essential raw materials for device fabrication technology. Their availability has been critical to production of epitaxial layers of device quality and to the successful functioning of fabricated devices. Gaseous chemicals are key starting materials for device fabrication by chemical vapour deposition, metal organic chemical vapour deposition, liquid phase epitaxy and vapour phase epitaxy. Other volatile chemicals are used as carrier gases, vapour transport agents, dopants and for atmospheric control during semiconductor processing.

The aim and the purpose of the project /part 11.03/ was :

1. To establish the capability to measure ppb levels of trace metals in electronic grade high purity gases at BSGRI.
2. To obtain analytical accuracy in the aforementioned which is equivalent to that of the most advanced level in the world.

The main duty of the Job description and objective was to develop the capabilities of BSGRI personnel to set-up, operate and utilize the atomic absorption apparatus as follows :

1. Introduce a sampling system for the measurement of trace metals in gases recognizing the problems associated with flammable, explosive and toxic compounds.
2. Introduce the techniques for the measurement of ppm trace metals using flame AAS and flameless AAS for ppb levels of trace metals in gases.
3. Introduce the techniques to separate the trace metals from the major metals in a matrix.

The project started in the year 1986 and now is lasting one year. During this period there were two UNIDO experts working on the project :

Willard L. Ent, Chief Technical Adviser

Juraj Berčík, expert in Atomic Absorption Spectrography

Activities program prepared by BSGRI on the bases of Job Description is in annexe 1.

Recommendations

1. In order to complete the establishment of research centers it is recommended to buy the following advanced instruments :
  - a/ Emission spectrometer /ICP System/
  - b/ Particles counter of the medium
  - c/ Ion Chromatograph for determination of trace anions /ppb levels/
  - d/ Differential pulse polarograph including stripping analysis /DPP, ESA/
  
2. To enable short-term and long-term fellowship training and study tours for operators in the field of trace analysis especially in the field of their application in trace gas analysis

# 1. POSSIBILITIES AND UTILISATION OF AAS IN TRACE AND ULTRA-TRACE ANALYSIS IN BSGRI

## 1.1 BSGRI - ANALYTICAL DEPARTMENT ORGANIZATION AND PROGRAM

BSGRI is headed by Director Chen Jinming who is the head of the whole project. Based on the project targets, the BSGRI will establish the following research centres :

1. Analysis and Inspection Centre for Specialty Gases
2. The Secondary Mass Transfer Centre of National Standards
3. Safety and Protection Supervising Centre for Specialty Gases.

The electronic industry requires high purity electronic gases with extremely low metal content, hence there is requirement of metal impurity analysis at ultratrace levels /ppm, ppb and below/.

BSCRI - Analytical Department has the following analytical sections :

- Section of Chromatography
- Section of Gas Chromatography GC/MS
- Section of Spectroscopy

Laboratory for trace element handling /Clean Room/ is simultaneously laboratory for atomic absorption spectrophotometry. From the point of view of contamination this is of course not the best solution. Laboratory is situated on the first floor in a new modern building. Clean room - laboratory has the vertical laminar airflow and about the US Federal Standard 209 B is classified as Class 100. The class number is the maximum allowable number of particles larger than 0.5  $\mu\text{m}$  and smaller than 5  $\mu\text{m}$  per cubic foot of air /about 28 liters/.

Laboratory is equipped with a new modern atomic absorption spectrophotometer Perkin-Elmer Model 3030 B manufactured in U.S.A. It is a doublebeam system, computer controlled with flame and flameless graphite tube atomiser and mercury hydride system. The instrument was installed and adjusted, but for



practical application has not yet been utilized. Mastering these high level techniques requires of course more time, especially in the case of utilising them in ultra trace analysis.

The head of the Section of AAS is Madam Chen Zhi Fen who studied at the Beijing University and finished her study in the year 1963. Three other workers are :

1. Assistant Engineer Li Shang, who studied physical chemistry at the Lanzhou University and finished his study in the year 1984.
2. Assistant Engineer Liu Qing Chin, who studied physical chemistry at the Nankai University and finished his study in the year 1986.
3. Miss Fan Jin Wen, who studied analytical chemistry at the Chemical Institute of Technology in Beijing and finished her study in the year 1983.

On the photograph /from left to right/ there are :  
Ms Chen Zhi Fen, Mr Berčik /expert/, Mr Guo Bing Chen /professor and translator/, Ms Fan Jin Wen, Mr Li Shang and Mr Liu Qing Chin.



## 1. 2 ATOMIC ABSORPTION SPECTROSCOPY IN TRACE AND ULTRATRACE ANALYSIS

Atomic absorption spectroscopy is one of the accepted techniques for metal analysis in the analytical laboratory. Several methods of metal atom vaporization are used in atomic spectroscopy with graphite furnace, flame atomization and mercury hydride system being three of the most widely used. The GFAAS technique provides minimum detection levels of sub-ppb, while the flame atomization method is in the low ppm range. Although advances have been made in the GFAAS and FAAS techniques, some problems and difficulties can still be encountered, such as sample matrix related problem, gas-borne particle analysis problem/normally the sample in GFAAS can be introduced into the graphite hollow tube furnace only as a liquid or as a solid/.

The means whereby the utilization of atomic absorption apparatus were reached were mainly through lecturing and discussing. The curriculum of lectures is given in annexes 2 - 8.

## 2. DETERMINATION OF TRACE METAL IMPURITIES IN ELECTRONIC GRADE HIGH PURITY GASES

There are a large number of specialty gases /about 35/ and for simplification they are usually categorized by chemical functionality and reactivity. The six specialty gas categories include silicon - precursor gases, dopants, plasma etchants, reactant gases, atmospheric /purge cylinder gases, as well as a final category designated "other" specialty gases.

Silicon-precursor gases such as silane and dichlorsilane are used in epitaxial and chemical vapor deposition processes to deposit layers of silicon, or silicon compounds /i. e. silicon dioxide, silicon nitride/ onto silicon substrates.

Dopants like arsine, phosphine and diborane are used as a source of controllable impurities within semiconductor de-

vices to modify local electrical properties of the medium, or to alter the characteristics of films.

Plasma etchants encompass a wide variety of halocarbon and fluorine-based gases, but carbon tetrafluoride is probably the most commonly used plasma etch gas.

Reactant gases include ammonia and hydrogen chloride /HCl/. Ammonia is used as a source of nitrogen in the production of silicon nitride layers in chemical vapour desposition. HCl is used to polish and etch wafers prior deposition steps by removing defects on the wafer surface due to mechanical polishing and handling of the wafer.

Atmospheric/burge cylinder gases - nitrogen and other atmospheric gases /including helium/ appear in this category. These gases are primarily used for purging certain processing systems and equipment.

"Other" specialty gases - tungsten hexafluoride is one example of this category. It is used as a source of tungsten for the deposition of tungsten silicide, which is used as an alternative interconnect material in VLSI devices.

The review of the most toxic hazardous and reactive gases is in the table 1 /Annex 8/. These gases are used for chemical vapour deposition, for ion implanting, doping, epitaxy and etching. The impurities which should be controlled are in the right of the table.

These gases require special sample handling techniques to prevent dynamic changes in composition due to reactivity with atmospheric moisture, air, or because they are corrosive or extremely poisonous.

Specific procedures must be developed for the analysis of ammonia, arsine, phosphine and silane. Individual instrumentation and safe handling systems need to be dedicated solely to each gas. Development of procedures for the convenient and reliable characterization of these reagents are much needed and would be noteworthy analytical contributions.

Due to extreme toxicity or other hazards, the working atmosphere must also be controlled to prevent intolerable levels of arsine, phosphine and the silanes. Extraordinarily

sensitive techniques are required for determining the presence of these gases at the ppb level in the work space atmospheres of semiconductor processing facilities.

### Contamination

All these high purity gases are primarily contaminated during storage, transportation and metering. Metal impurities are of particular importance due to their potential electrical activity in the forbidden band. Many of the components of the delivery system can generate particulates which may be many times the level of that in the filter effluent stream. Some of the causes of particulate contamination are walls of the piping system and gas cylinders, changing in the pipeline velocity, vibration of piping system, sampling valve, leaks and any mechanical device in the piping system. Hence gas-borne impurity particles analysis at ultratrace levels is important for electronic gas purity validation.

## 2. 2 THE PROBLEM OF SAMPLING AND COLLECTING OF GAS-BORNE PARTICLES FOR TRACE METAL ANALYSIS

The metal impurities concentrations in high purity gases for microelectronics are on the level lower than  $10^{-5}$  mass percent /e. g. 15 ng/l in a 10 Vol % phosphine mix/. Analysis of such materials requires a reproducible method of sampling and collecting /separation and concentration/ of particulates from the matrix. The sizes of such particulates are between 0.01 to 2  $\mu\text{m}$  or more and the smaller the particulates the greater the stability and lifetime of aerosol.

Sampling system for gas-borne particles generally consist of three parts:

- a means of collecting a gas sample
- a device to trap the particles and
- a means of measuring the amount of gas sampled.

The technique for collecting air-borne or gas-borne particles are based on one of the following principles: filtration, impaction, sedimentation, centrifugation, thermal precipitation, electrostatic precipitation and solvent wash.

Filtration and impaction are the most frequently used methods. The success of separation and collection of gas-borne

particles depends on: a/ purity and efficiency of the filtering or trapping medium; b/ low background contamination; c/ reasonable volume sampling; d/ sensitivity of the used analytical method.

#### 2. 2. 1 PURITY AND EFFICIENCY OF THE FILTERING OR TRAPPING MEDIUM

Filtration assembly consist of a sampling head, filter and the pump. There are several types of filters: Depth filters, membrane filters, filtration through graphite. While such sampling and collecting media are widely used, the problem originates from the fact, that the filter materials exhibit significant residual blanks for a number trace elements of interest. The existence of these blanks does not present a serious problem if long term, high volume sampling is used to collect sufficient sample to render the blank contribution negligible / 20 - 50 L/. However in relatively clean gases the use of such collection materials may necessitate inordinately long sampling periods. To achieve consistent and low background levels it is necessary to reduce contributions due to solvents, glassware, handling etc. and the filters' material must be precleaned before use. Many problems concerning trace and ultratrace analysis were discussed and lectured /annex 6/.

#### 2. 2. 2 LOW BACKGROUND CONTAMINATION

The first step in contamination control is "clean" sample preparation. Due to reactive and hygroscopic nature of some dopants, direct analysis without handling, transfer and sample preparation would be the preferred approach to avoid potential contamination from surfaces or reagents. Unfortunately most analytical techniques necessitate sample handling and preparation and a wide range of precautions are required (clean room, glove box with an atmosphere of argon or nitrogen containing less than 1 ppm of water and oxygen).

### 2. 2. 3 SAMPLING VOLUME/TIME

The minimum sample volume required to obtain a reasonable AAS analytical signal can be easily calculated using the characteristic concentration of the element.

### 2. 2. 4 DISSOLUTION OF SOLIDS ON FILTERS OR IN TRAPPING MEDIUM

The particulate matter collected on the filter has to be dissolved for analysis. Wet or dry ashing procedures are used. Although numerous procedural variations for this operation exist, some elements often cannot be subjected to dry ashing due to their high volatility. For wet-ashing procedure depending on the element analyzed and the AA techniques used, various acid concentrations and mixtures may be utilized.

## 3. SEPERATION AND COLLECTION OF PARTICLES BY SOLVENT WASH

### 3. 1 NITRIC ACID WASH

Kuzmin /Elektronnaja tehnika, Ser. 6, 94 /1974/; Ž. Analit. Chimi, 24, 429 /1969// proposed a method in which the elements Cu, Fe, Co, Pb, Ni, Bi in phosphine /PH<sub>3</sub>/ and arsine /AsH<sub>3</sub>/ are separated by nitric acid wash /6 vitreous silica absorber with 25 ml HNO<sub>3</sub>/. Active components arsine and phosphorus are oxidised to arsenic /H<sub>3</sub>AsO<sub>4</sub>/ and phosphoric /H<sub>3</sub>PO<sub>4</sub>/ acids and metal impurities are dissolved. The resulting H<sub>3</sub>PO<sub>4</sub> - HNO<sub>3</sub> solutions were connected and at 100° C evaporated in order to prevent the building of disturbing higher phosphoric acids. There is, of course, the danger of loss of some elements especially of Pb, Mn, Sb, Ti, and Sn. Contamination during this acid digestion and evaporation may result in introduction of systematic errors due to the high blank.

### 3. 2 WATER WASH

Kochler /Chem. Techn. 37, 103 /1985// proposed a method in which the elements are separated by water wash without reaction of the matrices PH<sub>3</sub>, AsH<sub>3</sub> and SiH<sub>4</sub>. For trapping

the particles serves a device composed from six ground inverted decomposable fused silica scrubber /to prevent contamination is the outer ground joint socked about the inner ground joint cone/ with inlet capillary of 0,5 mm diameter. Every scrubber was with 25 ml of high purity water filled. In the case of trapping the boron addition of 330 ug of mannitol was made. The pH 10 of the solution was adjusted with ammonium hydroxide and oxygen, by passing of high purity hydrogen, was removed.

In the case of monosilan undecomposable scrubbers placed in a clean hood with inert gas atmosphere were used. Alkali ions must be excluded.

Before analysis the sample bottles /cylinders/ in order to reach homogeneity were 10 minutes rolled and then the gas /30 to 60 l/ was through a special gas reducing valve sampled at a rate 25 l/h; In the end the apparatus was rinsed out with hydrogen. Washing solutions were then collected and before spectrometric analysis concentrated by evaporating. Evaporation in closed chambers purged with clean air continues to be the preferred concentration technique. Contamination from heating apparatus and the evaporation vessel can be reduced and effectively controlled.

The delivering of  $\text{PH}_3$  and  $\text{AsH}_3$  can be done with a connected absorptive apparatus with  $\text{HNO}_3$ ;  $\text{SiH}_4$  is air burned.

If 50 l of gas are used the relative detection limit by an OES collector technique amounts to 10 ng/l. The average error of determination of a single value amounts to between 10 to 80 %.

The success of separation and collection of gas-born particles for trace metal analysis depends on these factors:  
first - purity and efficiency of the filtering or trapping medium  
second - low background contamination enables low volume sampling in the case of using a sensitive analytical method for accurate determination.



MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS  
STANDARD REFERENCE MATERIAL 1010a  
(ANSI and ISO TEST CHART No. 2)



#### 4. PROBLEM OF DIRECT DETERMINATION OF GAS BORNE PARTICLES WITHOUT SEPARATION AND COLLECTING

Direct analysis in ultratrace region without handling and sample preparation should be the preferred approach to avoid potential contamination. Only GFAAS provides the possibility of analysis in this concentration region. Problem is how a gas sample, which is toxic and explosive, could be injected into the graphite tube furnace at the atomizing temperature.

#### 5. CONCLUSION

Analysis of gas borne particles can be made:

1. by separating the solid particles by filtration through a membrane filter /cellulose, glass or plastic material/
2. or through a porous graphite cup or cylinder .

In the former method the determinations are made by transferring the whole part of the filter into a suitable atomisation cell, whereas in the latter technique the graphite filter also serves as the atomization cell. Gas borne particulate matter can also be collected electrostatically in a graphite tube which is then transferred into the heating circuit for atomisation.

3. by separating the solid particles by solvent wash and using the evaporation technique and the normal liquid technique for atomisation.
4. Direct analysis of gas borne particles is teoretically possible , but it needs more time for research.

## Annex 1

### Activities programm of expert in atomic absorption spectro- photometrie

21. 8. Arrivel in Beijing /4.00 p. m./  
Project manager meets Mr. Berčik at Beijing Interna-  
tional Airport
22. 8. Introducing with BSGRI  
Introducing with Perkin Elmer 3030 AAS
24. 8. Introducing the various analytical methods for mea-  
suring trace impurities /Annex 2/  
Visiting UNDP resident office
25. 8. Lecture on advanced theory and operating technique of  
flame AAS and flameless AAS /Annex 3/
36. 8. Experiment - Measuring ppb level metal by using flam-  
less AAS and discussing
27. 8. Selection and optimisation of AAS operat ng conditions  
/Annex 4/
28. 8. Sampling system for the measurement of trace metals  
in flammable and toxic gases /Annex 5/.
29. 8. Go outing
31. 8. General problems in trace and ultratrace analysis  
/Annex 6/
1. 9. Electroanalytical methods in trace analysis
2. 9. Advanced analytical instruments in gas analysis /Annex  
7/ Lecture for the whole institute.  
Departure from Beijing 21.30

## Annex 2

### Curriculum of lecture:

Introducing to various analytical methods for measuring trace impurities

1. Trace and ultratrace level
2. Sensitive techniques used in inorganic trace analysis
3. Metrological parameters of analytical methods
4. Atomic emission spectroscopy
5. Inductivity coupled plasma AES
6. FAAS and GFAAS
7. Spark source and ICP mass spectrometry
8. Neutron activation analysis
9. Substoichiometric isotope dilution method
10. Differential pulse polarography
11. Stripping voltammetry

Annex 3

Curriculum of lecture:

ATOMIC ABSORPTION SPECTROPHOTOMETRY

1. Princip of AAS
2. Relation between atomic absorption and concentration
3. Atomization of sample
4. Comparison of FAAS and GFAAS
5. Methods to correct background absorption
6. Instrumentation
7. The flame atomizer
8. Spray chamber assembly and the burner
9. Sample introduction
10. Electrothermal atomisation
11. Vapour generation techniques

## Annex 4

Curriculum of lecture:

### SELECTION AND OPTIMISATION OF AAS OPERATING CONDITIONS

1. Sensitivity and characteristic concentration in AAS
2. Furnace operating conditions
3. Drying
4. Dry/Ash control
5. Atomisation
6. Preparation of atomise curve
7. Preparation of ashing curve
8. Tube cleaning
9. Interference effects in AAS
10. Matrix effects
11. Stable compound effects
12. Overcoming chemical interference effects

Annex 5

Curriculum of lecture:

THE PROBLEM OF COLLECTING GAS - BORNE PARTICLES FOR TRACE METAL ANALYSIS

1. Introduction
2. Sources of gas contamination
3. Size of particulates
4. Metal impurities concentrations in high purity gases
5. General scheme for inorganic trace analysis
6. Sampling system for gas-borne particles
7. Impactors
8. Filtration
9. Sampling volume/time
10. Calculating the minimum sample volume
11. Dissolution of solids on filters
12. Ashing of the filters

## Annex 6

Curriculum of lecture:

### GENERAL PROBLEMS IN TRACE AND ULTRATRACE ANALYSIS

1. Parameter which must be controlled in trace analysis
2. Contamination
3. Blank value
4. Detection limit
5. Control of contamination and loss
6. Airborne contamination
7. Clean rooms and clean hoods
8. Contamination and loss due to apparatus
9. Contamination due to reagents
10. Method of purification
11. Distillation and sub-boiling distillation
12. Isothermal distillation
13. Other sources of contamination and loss
14. Stability of standard solutions.

Annex 7

Curriculum of lecture:

ADVANCED ANALYTICAL INSTRUMENT IN GAS ANALYSIS

1. Purity monitoring
2. Bulk gases
3. Specialty gases
4. Purity specifications
5. Control of impurities in relatively chemically inert gases
6. Control of impurities in stable hydrocarbons
7. Control of impurities in toxic hazardous reactive gases



## Annex 8

## CONTROL OF IMPURITIES IN TOXIC HAZARDOUS GASES

<u>Reagent</u>		<u>Impurities Controlled</u>
Ammonia	$\text{NH}_3$	$\text{CO}$ , $\text{H}_2\text{O}$ , THC, $\text{H}_2$ , $\text{O}_2$ ,
Arsine	$\text{AsH}_3$	$\text{CO}$ , $\text{CO}_2$ , $\text{H}_2$ , $\text{N}_2$ , $\text{O}_2$ , THC, Total Sulfur, $\text{H}_2\text{O}$ , metals
Boron Trichloride	$\text{BCl}_3$	-
Boron Trifluoride	$\text{BF}_3$	$\text{O}_2$ , $\text{N}_2$ , $\text{SO}_2$ , $\text{SiF}_4$
Chlorine	$\text{Cl}_2$	-
Dichlorsilane	$\text{Cl}_2\text{SiH}_2$	$\text{SiCl}_4$ , $\text{SiCl}_3\text{H}$ , etc., As, B, C, Fe, P, $\text{Si}_2\text{Cl}_x\text{O}_y$
Flurine	$\text{F}_2$	-
Germane	$\text{GeH}_4$	$\text{AsH}_3$ , $\text{PH}_3$ , $\text{SiH}_4$
Hydrogen Chloride	$\text{HCl}$	$\text{CO}_2$ , $\text{H}_2$ , $\text{N}_2$ , $\text{O}_2$ , inert gases THC, $\text{H}_2$
Phosphine	$\text{PH}_3$	$\text{H}_2$ , $\text{N}_2$ , $\text{O}_2$ , THC, $\text{AsH}_3$ , $\text{CO}_2$ , $\text{H}_2$ , $\text{H}_2\text{O}$
Silane	$\text{SiH}_4$	$\text{CO}$ , $\text{CO}_2$ , metals, $\text{HCl}$ , $\text{H}_2$ , $\text{Cl}_x\text{SiH}_{4-x}$ , $\text{N}_2$ , $\text{O}_2$ , $\text{H}_2\text{O}$ , $\text{Si}_x\text{H}_{2x-2}$ , $\text{SiO}_x\text{H}_x$

THC - Total Hydrocarbons as  $\text{CH}_4$