OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.

DISCLAIMER

FAIR USE POLICY

CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org

RESTRICTED

DP/ID/SER.A/636
23 September 1985
ENGLISH

IMPROVEMENT OF TESTING AND EVALUATION FACILITIES
NATIONAL TEST HOUSE, CALCUTTA, PHASE II

DP/IND/82/007

INDIA

Technical report: Testing and analysis of industrial effluents *

Prepared for the Government of India
by the United Nations Industrial Development Organization,
acting as executing agency for the United Nations Development Programme

Based on the work of Guenter J. Eppert,
expert in testing and analysis of industrial effluents

United Nations Industrial Development Organization
Vienna

* This document has been reproduced without formal editing.

V.85-31247

ABSTRACT

This report is based on the project document "Improvement of Testing and Evaluation Facilities, National Test House, Calcutta - Phase II" within the scope of the United Nations Development Programme and deals with the testing and analysis of industrial effluents in India, DP/IND/82/007/11-02.

The objective of the activity for assistance and giving advice in setting up a complete instrument oriented testing laboratory equipped with modern instruments required for analysis of industrial effluents could be achieved within the scheduled three months (April to June 1985). The main conclusions and recommendations are the following:

1. In order to set up a laboratory working efficiently in the fields of testing and analysis of industrial effluents the present equipment at the National Test House (NTH) should be completed by a number of missing accessories and additional instrumentation (see summary of recommendations).

2. Two fellowships in the field of chromatography with qualification in water analytics should be urgently realised.

3. Measures are recommended to the Ministry of Supply and Rehabilitation of the Indian Government according to the proposals given in this report, concerning the present mode of sampling and effluent testing and the use of mobile laboratories as a first step in setting up a laboratories' network all over the country.

TABLE OF CONTENTS

INTRODUCTION

According to my duties I was familiarized with the present facilities and testing possibilities of the NTH, especially in the Chemical Division of the NTH.

The NTH deals with controlling and testing of products and materials in many disciplines, the Chemical Division with testing of metals, building materials, oils, fuels, paints, enamels, high polymers etc.

The chemical division is subdivided into nine sections, each headed by an Ass. Director.

The section "Chemical Standard Lab" investigates, e.g., pesticides, effluents, fertilizers, desinfectants, gases, and deals also with bacteriological tests. The setting up of a modern industrial effluents laboratory is planned within this Chemical Standard Lab and is already running in the first step of its realization. The first instrumentation was made available by the Government and UNDP. These instruments are partly in operation or have been installed and started during my stay.

The submitted report deals with the assessment of the now available equipment with regard to the growing demand of water analytics. Furthermore, it deals with topical problems in this field which were assessed in detail and thoroughly discussed in several chapters. The report involves recommendations for the next development and for the extension and improvement of water analytics, and in the analytics of industrial effluents, resp.

All this was attained in full agreement with the responsible and competent officials of the NTH who approved the report and the conclusions and recommendations.

SUMMARY OF RECOMMENDATIONS

1. The presently available equipment for testing of effluents should be completed by the missing accessories for the Atomic Absorption Spectrophotometer and the Gas Chromatograph/Mass Spectrometer System. It is recommended to procure test kits, journals and textbooks as soon as possible (for details see chapter I).

2. The existing equipment should be completed by two gas chromatographs and one liquid chromatograph and additionaly by accessories for gas chromatography. The current EPA-Methods should be procured from the USA as soon as possible (for details see chapter III).

3. Two fellowships abroad in the field of chromatography simultaneously with a training in mass spectrometry and in combination with water analytics seem to be urgently necessary.

4. The Indian Ministry of Supply and Rehabilitation should consider the proposals for sampling and mobile test laboratories, given in chapter IV.

5. Procurement of a Sapromat, a TOC-Analyzer and a Clark-Electrode (for details see chapter V).

I. THE PRESENTLY AVAILABLE EQUIPMENT AT THE CHEMICAL DIVISION OF THE NTH FOR TESTING AND ANALYSIS OF INDUSTRIAL EFFLUENTS

The now existing modern equipment for testing and analysis of industrial effluents and water samples include the following instruments:

1 Atomic Absorption Spectrophotometer, procured by the Government;

1 Polarograph, procured by UNDP;

1 IR-Spectrophotometer, procured by the Government;

1 UV/Vis-Spectrophotometer, procured by the Government;

1 On-line Gas Chromatograph/Mass Spectrometer System, procured by UNDP.

The Atomic Absorption Spectrophotometer, Model 370, dates from 1979 and has been delivered by Perkin Elmer.It is fully installed and in operation. Though the instrument is not the newest type it can be used very advantageously and time-saving for the most urgent determinations of metals in different waters. Nitrous oxide required to achieve higher flame temperatures is not available to date. In spite of this, e.g., all for drinking water relevant elements can be automatically determined, except aluminium and silicon but inclusive lead, copper, zinc and cadmium.

The following parts belong to the supply: A burner, a nebulizer and a number of hollow cathod lamps. Unfortunately, efficient accessories are missing such as the Arsenic-Selenium Sampling System for the hydride technique and the Flameless Mercury Analysis System (mercury vapour technique), as well as the very versatilely applicable graphite furnace. In most cases the graphite furnace technique very strongly extends the sensitivity of the determinations. The supplied standard methods for atomic absorption spectrophotometric analyses date back to 1973.

The polarograph, Model 3051 from Sargent-Welch Sc. Co., USA, is also in operation and can be used for determinations of metal traces and several organic compounds. The instrument

incorporates facilities for the conventional DC - polarography such as hanging drop electrode and dropping mercury electrode, likewise stripping techniques (inverse polarography) which can be used very conveniently in trace analysis by enrichment of small quantities of metals.

The IR-Spectrophotometer has been manufactured in 1983 by Perkin Elmer and represents a new highly efficient spectrophotometer. Because of a defect in the electronics it was not possible to put it into operation during the time of my stay; the service was not able to repair it within this time.

The instrument incorporates facilities like a double beam ratio-recording, automatic wave number correction and data handling. It operates within the wavelength range of 180-5000 cm^{-1}. On principle, this spectrophotometer can be combined with modern computers and data systems. The equipment is to be used to identify and determine most of the groups and classes of organic compounds; preferably it is not suitable in the range of lower levels as this is true of all instruments of the dispersive type.

The quantitative determination of several types of hydrocarbons in waste water $\geq$ 0.1 mg/l after their enrichment by extraction and column chromatographic removal of interfering compounds represents a well known application of IR spectroscopy in the waste water analysis. The method was introduced according to DIN 38409.

The Varian UV/Vis spectrophotometer is an automatically recording instrument of the newest construction, scanning within the range of 185-900 nm with an accuracy of $\pm$ 0.2 nm, a resolution of 0.07 nm and a maximum scan speed of 10 nm/s. It is equipped with recorder and monitor screen, as well with a purging device when making measurements below 200 nm. A microprocessor system allows programming and controlling of the instrument through the usual keyboard. The first and second derivative of the spectrum can be recorded to further enhance spectral details, as well as the logarithm of the signal in the case of low absorbance peaks.

The Gas Chromatograph/Mass Spectrometer System HP 5995 from Hewlett Packard can be considered as the state of the art in the field of moderate price instruments which gives versatile benefits. Unfortunately, during the first time of my stay, the cooling system was missing and, therefore, no start up was possible. After the installation of the cooling system the serviceman of Hewlett Packard did not come in spite of several urgent reminders.

Main features of the system are the highly reliable and versatile quadrupole, the proven electron impact source, the sufficient mass range of 10 to 800 AMU with a resolution of 1 AMU and linear mass scale, as well as the autotuning and the data acquisition and processing.

The included capillary gas chromatograph possesses a combined split and splitless capillary injector. The column oven temperature can be varied with programming between - 50 to + 350°C.

Concerning the so-called library search which is very important to solve identification problems, it seems to be urgently necessary to complete the presently available two libraries (tapes) for drugs and pollutants.

Actually, this Gas Chromatograph/Mass Spectrometer System is the most important equipment in connection with the problems of industrial effluent analysis and the identification of priority pollutants, particularly, in the range of trace levels. This statement will be emphasized by chapter II.

RECOMMENDATIONS TO CHAPTER I

1. Procurement of the missing accessories to the Atomic Absorption Spectrophotometer from Perkin Elmer including

a) the Arsenic-Selenium Sampling System

b) the Flameless Mercury Analysis System

c) the HGA Graphite Furnace.

All options have to be adjustable to the Model 370. In case c)

the unit HGA 500/400 with the necessary programmer unit has to be ordered. Furthermore, the newest collection of Analytical Methods for Atomic Absorption Spectroscopy should be purchased from Perkin Elmer.

2. Procurement of additional libraries for organic compounds, especially, for Priority Organic Pollutants, to be utilized for the Model GC/MS System 5995 from Hewlett Packard.

3. Procurement of test substances and Standard Kits of Priority Pollutants according to Supelco International Catalogue. This is necessary to establish an own library for spectra and retention indices.

4. Subscription for relevant journals and procurement of selected textbooks in the field of chromatography and water analytics (titles were listed and handed over to NTH).

II. THE INSTRUMENTAL POSSIBILITIES IN THE CHEMICAL DIVISION OF NTH IN VIEW OF THE PROBLEMS WHICH ARE TO BE EXPECTED WITH THE IDENTIFICATION AND QUANTITATIVE DETERMINATION OF PRIORITY ORGANIC COMPOUNDS AND CLASSES OF COMPOUNDS IN INDUSTRIAL EFFLUENTS

The identification and determination of relevant classes of organic compounds and priority pollutants in waste waters of industry and other sources are one of the most complicated and difficult problems in analytics. Many central institutions all over the industrialized countries deal with these problems. The investigations are very expensive and are conducted with a great number of instruments and personnel.

In spite of this, up to now there is no general and entirely complete pattern of analysis or of pretreatment of water samples. It is rather necessary to select and restrict the corresponding analytical measures from problem to problem.

The first step of analysis is always a well designed procedure of enrichment and concentrating. Subsequently, a separa-

tion process must be used, in any case. It is the chromatography which meets all requirements best.

Through a lot of priority organic pollutants, being under discussion, are separable and determinable by the most advanced methods of gas chromatography, it must be emphasized that the pollutants governed by this method often cover only the smaller part of organic matter in waters and effluents.

It is well known that only about 20 % of the two million organic compounds known to man is investigable by gas chromatography. By the way, about 500 of them have been already identified in drinking water to date.

Accordingly, the remaining 80 % of compounds is to be separated and determined by the methods of liquid chromatography which develops with vast speed but as yet is not quite so advanced in the means of detection and identification as gas chromatography.

In a few words, this is the situation with which everybody is confronted in the case of analysis of complex mixtures of organic compounds in water.

The problem, however, considerably simplifies with regard to industrial effluents of known composition from single enterprises. Because the main profile of that enterprises mostly is well known to the test personnel, the control can be simplified.

Annex A of this report contains a number of important classes of organic compounds frequently found in industrial effluents, river water and partly in ground and drinking water. If we are considering the methods of determination (last column of the table, annex A) it seems evident and underlines the above assertion that chromatographic methods are dominating, first of all, gas chromatography using a number of special and selective detectors.

In this connection, quadrupole mass spectrometers of modern construction can be considered as special and very versatile gas chromatographic detectors. Therefore, we find relatively simple Mass Selective Detectors (MSD) on the market, e.g., the MSD HP 5970B, offered by Hewlett Packard.

The pre-eminence of gas chromatography in the waste water analytics results not at last due to the highly developed capillary column technique, that resolution and efficiency are widely superior to that of packed columns. However, in many cases especially of industrial waste waters of known composition or limited number of compounds packed columns can be very convenient and fully sufficient.

The modern liquid chromatography (HPLC = High Performance Liquid Chromatography) supplements gas chromatography in an ideal manner and replaces several not so convenient gas chromatographic methods. For future, as has already been stated, an important potential of liquid chromatography lies in the wide field of non-volatile compounds in water.

A considerable advantage of liquid chromatography is the fact that aqueous samples can be injected directly onto the columns in contrast to gas chromatography, especially,if gas chromatography is coupled with a mass spectrometer detector because mass spectrometers are very sensitive to water.

In many cases the liquid chromatographic columns can be used directly for the enrichment procedures, since liquid chromatography uses advantageously aqueous organic systems.

All this states clearly that the available gas chromatograph/mass spectrometer system will never be adequate to solve the problems with which NTH will be confronted.

RECOMMENDATIONS TO CHAPTER II

Extension and improvement of the existing equipment according to the proposals of chapter III.

III. ADDITIONAL MODERN INSTRUMENTATION WHICH WILL URGENTLY BE REQUIRED FOR AN EFFECTIVE ANALYSIS OF INDUSTRIAL EFFLUENTS

According to the explanations in chapter II, it should be clear that the gas chromatographic equipment must be further completed.

Because the problems to be expected will be very different and complicated (annex A), several detectors must be used simultaneously. In future, therefore, two modern gas chromatographs are necessary.

As a recommendable type, I wish to mention the Gas chromatograph 5880 A from Hewlett Packard. Apart from the obligatory thermal conductivity detector, this instrument is equipped with a flame ionization detector (FID), a nitrogen-phosphorus detector (NPD), an electron capture detector (ECD), and a flame photometer detector (FPD). The latter detectors are selective detectors to nitrogen and phosphorus containing compounds, resp., to compounds with high electron affinity such as halogens, conjugated =CO, -CN, $-NO_2$, metallic organic compounds, pesticides and polychlorinated biphenyls, resp., are highly selective to sulphur or phosphorus (FPD).

Also a Hall electrolytical conductivity detector is adaptable to the apparatus 5880 A which can be made selective to halogens, or sulphur, or nitrogen.

Four detectors can be installed at the same time. The comfort to the identification by means of the inserted, so-called basic programming is considerable. In the case of samples with unknown provenance, all already previously identified compounds can be recognized easily.

The common techniques of split, splitless and "cool on column injection" are available, as well as, of course,a temperature programming and fully automatic evaluation methods.

The splitless injection is the most efficient injection method in waste water analysis by capillary gas chromatography.

Another important accessory is the Purge and Trap Sampler

for the concentration and analysis of volatile low-boiling substances as halocarbons, etc. (annex A).

In the case of not too high-boiling hydrocarbons the accessary "PNA-Analyzer" (PNA = paraffines, naphthenes, aromatics) is useful for automatic realizing the compound class analysis of such mixtures.

As has been already mentioned, likewise, the introduction of the high performance liquid chromatography has to be realized, as an important supplement of gas chromatography, with many potentialities in the analysis of industrial effluents and waste waters.

In this connection instruments are coming into question like the type HP 1090, offered by Hewlett Packard. Of course, there are many other types of apparatuses with high efficiency on the market, e.g., from Perkin Elmer, Varian, Du Pont, and other companies. It is advisable, however, for service, spare part stock-keeping and software to cooperate with one partner only; and even the basic existing GC-MS system has been supplied by Hewlett Packard.

The HP 1090 instrument is advantageous, first of all, due to its diode-array detector which easily allows to confirm the purity of each peak and the identity of the compounds by automatic spectral recording. Every point of the chromatogram immediately delivers a complete UV-spectrum and the peak-sensitivity may be individually optimized for trace analysis by computer.

To the apparatus included microbore columns ensure a very low solvent consumption which is extremely important for low costs of analyses and also for the laboratory security, because handling of organic solvents always involves certain hazards.

RECOMMENDATIONS TO CHAPTER III

1. Procurement of two gas chromatographs,

type HP 5880 A (universal system),
type HP 5890 A.
1 liquid chromatograph,
type HP 1090.
Supplier: Hewlett Packard, USA.

2. Arranging of two fellowships,
1 fellowship in the field of gas chromatography,
1 fellowship in the field of liquid chromatography.

3. Inquiry for Application Notes in the fields of investigation of waste water and environmental pollution by means of gas chromatography, GC-MS and liquid chromatography to Hewlett Packard.

4. Procurement of most versatile liquid phases and solid supports for gas chromatography (listed and handed over to NTH).

5. Procurement of the current EPA-Methods from the Environment Protection Agency, USA:
"Identification of Organic Compounds in Effluents from Industrial Sources".
"Methods for Chemical Analysis of Water and Wastes".
"Guidelines Establishing Test Procedures for the Analysis of Pollutants".
"Sampling and Analysis Procedures for Survey of Industrial Effluents for Priority Pollutants".
"Analysis of Pesticides Residues in Human and Environmental Samples".
Inquiry:
US EPA Effluent Guidelines Division, Washington, DC, 20460
and National Technical Information Service (NTIS) 5285, Port Royal Road, Springfield, VA 22161

IV. SAMPLING AND TRANSPORT OF EFFLUENTS

With the promulgation of the Water Act for prevention and control of pollutants in India in 1974 the NTH and its subordi-

nated Laboratories in Bombay, Madras and Chaziabad (near Delhi) have to control industrial effluents and river pollutions all over the country.

At present, Industrial Laboratories are sending samples, e.g., to NTH which tests them according to the existing Indian Standards. They do not contain methods for the identification and determination of classes or individuals of organic compounds.

Virtually, there is no guarantee for the control, neither that of sampling (selection of representative samples) nor of gaining a statistical survey on water pollution, just as there is no possibility to control the handling and transport of samples.

In connection with organic pollutants the transport of samples over large distances involves serious problems. Most samples change very rapidly, after some time the determined composition does not reflect the original one.

An effective regular sampling should be done by NTH and the subordinated institutions themselves via personnel which is specially trained for sampling. For relevant places, automatic sampling devices can be installed later on.

In future it will be inevitable to transport the samples by special cars which allow a cool sample storage at $4^{\circ}C$ to prevent changing.

In this connection the use of so-called mobile laboratories, i.e., of vehicles with a fixed installed equipment for the most urgent determinations and measurements should be thoroughly discussed. This way is essentially less expensive than the establishment of a network of laboratories, measuring places, equipment etc., between the main testing laboratories and, therefore, will be reasonable at least at the beginning.

Moreover, it seems to be a very effective way for analytical controlling of outfalls (rivers) on the spot to charter proper ships in which then even rather sophisticated instruments can be installed. A wide spectrum of methods according

to the size of the "floating laboratories" can be used in testing without time delay.

If such facilities could be realized, a general survey about the pollution of the main rivers would be achieved. Municipal, industrial and other influxes in highly populated areas would come under effective governmental control.

RECOMMENDATIONS TO CHAPTER IV

The proposals given in chapter IV should be considered by Indian Governmental Institutions.

V. SETTING UP AND ORGANIZATION OF MODERN LABORATORIES FOR QUALITY CONTROL OF INDUSTRIAL EFFLUENTS AND WATERS

The continuously growing demands on the NTH in connection with the intensive analytics of industrial effluents, surface waters, as well as ground and drinking water, require several preconditions, which will be dealt with below.

A. Necessary improvements at the NTH

Extension of testing and strengthening of specialization

Nowadays, the problems of water control cannot be solved by chemical methods alone. A known content of organic and inorganic substances in water usually does not yield a sufficient information about toxicity. Not only because the toxicity of each substance often is not exactly known, moreover, the toxicity of effluents can be greatly influenced by interaction between individual compounds and dissolved minerals. It can change the essential microbiological fauna and flora in an inadmissable way. Therefore, these effects have to be evaluated directly

through biological and toxicological tests.

Proceeding from these facts a modern laboratory for testing and analysis of industrial effluents and water samples has to be subdivided into three sections. One laboratory section must be responsible for chemical methods, further subdivided into one laboratory that deals with instrumental methods, and a second one that has to practise the common wet chemical methods and the pretreatment of the samples or the enrichment procedures, resp.

The biological laboratory should be an independently working section in which biologists deal with the evaluation of microfauna and flora in outfalls (charged rivers etc.) revealing the influence of effluents on microorganisms.

And last not least, toxicologists must prove in a toxicological laboratory section the toxic properties of industrial effluents by means of fish-tests and tests on algae and bacteria.

Considering the present structure and distribution of tasks within the chemical division of the NTH, especially within the Chemical Standard Lab,one can conclude that a greater specialization should be realized step by step. Really, in any case, it is the only way to accomplish an efficient operation of such highly sophisticated instruments as spectrometers, GC/MS systems, chromatographs etc. Of course, this can be done not before the recommended supplement of the equipment has been provided and before the realization of new fellowships to get a qualified scientific personnel in view of the extended tasks.

Assessment of existing Standards for Testing of Effluents and Water

The available Indian Standards (IS) on Water Pollution Control were examined in view of the newest known international methods.

An assessment of the general tolerance limits for industrial effluents (IS 2490/1981),as well as of tolerance limits for industrial effluents of different industrial effluents of different industrial branches (IS 2490 series) discharged into inland surface water, public sewers, marine coastal areas or on land for irrigation purposes, will not be given here, because for this an exact knowledge of the special conditions within the country would be necessary. For this reason, it has been renounced a comparison with values from other countries or international recommendations. The following discussion, therefore, only deals with the methods of Sampling and Test for Industrial Effluents (IS 2488, Part I-V, 1966, 1968, 1976) and IS 4733/1972, the latter for Sampling and Test of Sewage Effluents.

These standards include most of the internationally used methods. Nevertheless, one of the important summary parameter for the evaluation of waste waters, the so-called total organic carbon (TOC), is missing. Only the Biological Oxygen Demand (BOD_5), IS 4733/1972 and IS 2488 (Part I), and the Chemical Oxygen Demand (COD), IS 2488 (Part V), are standardized according to the usual wet chemical methods.

Within the other methods for inorganic and organic compounds colorimetric methods are dominating. Except sulphide (titration), chloride (Mohr, Volhard), sulphate and magnesium (gravimetry), calcium (complexometry) and sodium and potassium (flame photometry) all cations and anions are determined by means of colorimetric and photometric methods, resp. This holds true also of phenols and the pesticides Parathion and Malathion, whereas the chlorinated hydrocarbons DDT, BHC (hexachloro-cyclohexane), Lindane, Aldrin, Dieldrin and Endrin are determined converting the organic chlorine using metallic sodium into chloride, estimated by Volhard's method.

With the purchased atomic absorption spectrophotometer it is now possible to determine all metals included in the standards very quickly and accurately. In the case of boron, the

graphite furnace recommended in chapter I will be necessary. In future the determination of all mentioned pesticides should be realized by gas chromatography,as well as the determinations of phenol mixtures.

In addition, the present equipment should be completed by automatic methods for the determination of BOD and TOC (as mentioned, this determination has not been introduced up to now) which operate quickly and exactly. In the case of BOD the Sapromat is a recommendable apparatus, basing on coulometric oxygen deficit measurements in the range of 1-4000 mg/l BOD; manufacturer: J.M.Voith, Heidenheim a.d.Brenz, FRG. The TOC-Analyzer is based on the thermocatalytic combustion of samples and the determination of the formed carbon dioxide by infrared measurement. The time for one analysis by the TOC analyzer amounts to a few minutes only,with a lowest limit of detection of about 0.5 mg/l carbon; manufacturer: Beckman Instr. Inc., USA. There are a lot of types of such instruments on the market, likewise including other chemical principles.

The COD may be further determined by the usual chemical method with potassium dichromate solution, however, a comparison with DIN 38409 or APHA is recommended.

Moreover, an Auto-Analyzer from Technicon GmbH can be taken into consideration, provided that a high number of samples are concerned. With such an equipment not only COD values are conveniently determinable, but also a considerable number of inorganic and organic compounds including detergents will be amenable to fully automatic colorimetric routine analysis.

The dissolved oxygen can be determined by the Winkler Method which is commonly introduced. However, more recommendable would be here a so-called Clark-Electrode. It is a membrane-electrode and, therefore, versatilely applicable without disturbance, even available in form of a probe for deep-sea research. The oxygen is reduced by means of a gold cathode to hydroxide ions, whereas silver is anodically oxidized and reacts with the electrolyte to silver chloride.

Finally, it may be pointed out that IS 2488, IS 4733 and IS 6582 in accordance with International Standards strictly demand a sample storage at 4^{o} C. This underlines the recommendations which were given in chapter IV.

B. Remarks on the setting up of a quality control system all over the country

Proceeding from the present state it seems difficult to propose a proper control system for quality control all over the country. First of all, the laboratories of the NTH,as well as in Bombay, Madras and Chaziabad should obtain a modern equipment and a sufficient analytical potential.

The next steps then must be the active control of factories and enterprises on the spot by sampling by trained personnel from the central institutions. As has been explained in detail in chapter IV the equipping of mobile analytical laboratories should be a suitable solution of the problem of control at the beginning. Afterwards, based on the gathered experience and findings, a number of smaller laboratories can be installed according to the existing industrial production density and effluent quantities. These laboratories should be able to carry out analytical routine, connected with effluent and water control, e.g., the determination of pH, dissolved oxygen, electrolytic conductivity, suspended solids, total residues, required anions and cations (heavy metals), total phosphate, total chlorine and nitrogen, as well as phenols, oils and priority organic compounds by means of simple methods, nowadays available. Of course, these laboratories should determine the COD, BOD, TOC and UV-extinction.

Altogether, the equipment of small laboratories will be not excessively expensive because all special determinations which need more sophisticated instruments concern the bigger central laboratories.

At that time then a reasonable uniformity of experimental

procedures and presentation of results should be introduced, because uniform methods and results will promote the accumulation of comparable data which should be the basis of charted classifications of rivers and waters all over the country.

A rigid standardization of the more complicated, special and versatile instrumental methods in the central laboratories seems for the time being not so desirable, for it would tend to defeat the aspired versatility of testings.

Proposals beyond this may be not reasonable at present. However, it should be clear that the above mentioned project has to be organized according to the example of the other industrialized countries.

RECOMMENDATIONS TO CHAPTER V

1. Procurement of an analyzer for the automatic determination of the Biological Oxygen Demand (BOD), e.g., the type Sapromat, supplied by J.M. Voith, Heidenheim, FRG.

2. Procurement of an analyzer for the automatic determination of the Total Organic Carbon (TOC), e.g., the type Beckman TOC-Analyzer, supplied by Beckman Instr.,Inc., USA.

3. Procurement of a Clark-Electrode for the automatic determination of dissolved oxygen, e.g., supplied by Wissenschaftlich-Technische Werkstätten, GmbH, Weilheim, FRG.

VI. SHORT REVIEW OF INTERNATIONAL TRENDS IN THE FIELDS OF TESTING AND ANALYSIS OF INDUSTRIAL EFFLUENTS AND WATERS AND CONCLUSIONS IN CONNECTION WITH THE SETTING UP OF A COMPLETE INSTRUMENT ORIENTED TESTING LABORATORY

On principle, experts agree that industrial enterprises have to bear investments not only for waste water purification

plants but also the costs for any equipment and current control of effluents in the same way. They have strictly to observe the stipulated thresholds otherwise appropriately high penalties may be imposed.

The random sample control applies to central institutions with the aim to prevent further and uncontrolled pollution of environment and gradually to lower the preliminary fixed limits of contamination. The central institutions have to establish a survey upon the respective extent of water pollution, i.e., upon content and distribution of priority pollutants within the controlled districts according to governmental decisions, acts and international recommendations.

More and more such assignments are basically supported by means of modern data processing which enables officials to get a comprehensive evaluation of data for judging the risks arising from internationally recorded priority pollutants, resp., poisonous substances requiring special attention in view of toxicity, carcinogenicity and persistence.

Proceeding from these requirements the methods of investigation in water analytics and the manufacture and designing of appropriate devices are developing very quickly appearing mainly two trends:

1. Application of highly sophisticated instruments to improve and exhaust all possibilities of reliable and comprehensive identification of priority pollutants with the aim of lowering their present detection limits, and avoiding separate concentration steps as far as possible.

2. Broad offering of automatically functioning devices for the determination of the common parameters for characterization of water and waste water qualities, in form of automatically operating laboratory instruments, as well as in form of automatic measuring stations on the spot, including long-distance data transmission.

Beside of these trends, successful efforts are being observed to market simpler methods (quick assays) by means of

portable kits for controlling of water quality on the spot. Available are complete test kits for a rapid colorimetric testing of relevant cations and anions, as well as test tubes to monitor water pollutants like pollutants in the ambient air. Further test paper strips for semiquantitative measurements due to different colour alterations are offered.

The trend in the development of highly sophisticated laboratory instruments, which are successively entering into water analytics, is being reflected by the application of such advanced methods as Multielement Ion-Coupled Plasma Emission Spectroscopy (ICP). It allows a fully automatic determination up to 15 elements per minute; also sulphur and phosphorus are determinable.

Modern Atomic Absorption Spectrophotometers use now the inverse Zeeman-Effect for an efficient background correction in the graphite furnace technique (Zeeman 5000 System, Perkin Elmer).

A second important analytical use of plasma represents the Microwave Plasma Detector (MPD) in gas chromatography. This is a specifically indicating sensitive detector of compound groups containing, e.g., the elements carbon, hydrogen, oxygen, nitrogen, chlorine, fluorine, and phosphorus, independently of the structure of their parent compound. By comparing elemental response ratios of unknown compounds with those of a standard, the empirical formula of the peak compound can be determined.

A further extension of the possibilities for identification in gas chromatography is given by the so-called Multidimensional Gas Chromatography (MGC) with capillary columns in double oven instruments (Siemens).

In mass spectroscopy super GC/MS systems are available with instantly switchable electron impact (EI) and chemical ionization (CI) source which allow a comprehensive identification. Now such mass spectrometers with soft ionization technique are also on line coupled with liquid chromatographs, equipping them with the detection power of mass spectrometry. Such investments are to be completed by versatile data systems to handle vast quantities of data and to carry out the evaluation and storage

of the results from a set of chromatographs and instruments.

Worth mentioning in connection with problems of identification are, of course, Fourier Transform IR Spectrophotometers, which open new possibilities in IR spectroscopy and overcome its relatively poor sensitivity. However, an on-line coupling with chromatography is limited now as before.

Several companies offer complete Water Pollution Analyzer Systems, for example, the Water Pollution Analyzer of Perkin Elmer or the Organic-In-Water Analyzer GC/MS System of Finnigan. The automatic Headspace-Injection Systems for volatile pollutants in water are to the point too.

In liquid chromatography the already mentioned Diode Array-Detector and the Micro Column Technique represent a considerable advance. The development in liquid chromatography concerns not only the wide field of organic compounds but also inorganic anions and alkali and alkaline earth ions by means of the so-called Ion-Chromatographs (Biotronic), especially in water.

At the present state of first steps in establishing a modern industrial effluent laboratory at the NTH the extension of the equipment beyond that already recommended is not advisable and reasonable. But the discussed trends demand to keep track of the further development and extension of analytical possibilities of the NTH and for the long-term qualification of the scientific personnel.

VII. FURTHER ACTIVITIES AND ASSISTANCE DURING THE STAY AT THE NTH

Besides the assessments and recommendations according to my assignment and the working plan, my activities dealt with discussions on technical topics and with assistance and advice to the start-up of the presently available equipment. Also special lectures were given on gas chromatography, liquid chromatography and water analytics (contents see annex B).

ANNEX A

(to chapter III)

Important classes of organic compounds in industrial effluents

Compound Class	Method according to EPA	Method of enrichment	Method of determination
(lower) Halocarbons	601/624	Purge and Trap	GC/HSD;GC/MS
(lower) Aromatics, Chloroaromatics	602/624	" "	GC/PID;GC/MS
Acrolein and Acrylonitrile	603	" "	GC/FID
(lower) Amines	+)	Strip and Trap	GC/FID
Phenols, Chlorophenols, Nitrophenols	604	Liquid/Liquid Extraction	GC/FID/ECD
Phthalate Esters	606	" "	GC/ECD
Nitrosoamines	607	" "	GC/NPD
Pesticides and Polychlorinated Biphenyls (PCBs)	608	" "	GC/ECD/HSD; LC/UV
Nitroaromatics	609	" "	GC/FID/ECD
Polynuclear Aromatic Hydrocarbons	610	" "	GC/FID; LC/UV/Fluor
Haloethers	611	" "	GC/HSD
Chlorinated Hydrocarbons (Aliphatic, Aromatic)	612	" "	GC/ECD
Benzidine and Derivatives	605	" "	LC/Electrochem.
2,3,7,8-Tetrachlorodibenzo-p-dioxin	613	" "	GC/MS
Phenols, Chloro-, Nitrophenols	625	Acid Extraction pH 2	GC/MS
Chlorinated Hydrocarbons, Aromatics, Nitroaromatics, Phthalateesters, Polynuclear Aromatics, Pesticides, Benzidine, Haloethers, Diphenylhydrazine, Nitrosodiphenylamine, PCBs and Dioxin	625	Base Extraction pH 11	GC/MS

Compound Class	Method according to EPA	Method of enrichment	Method of determination
Mineral Oils and Hydrocarbons	DIN 38409	Liquid/Liquid Extraction	IR
Strong Polar Organic Compounds, Carboxylic Acids		Adsorption by Polystyrene	GC/FID, LC
Lignosulphonic Acids	Special Methods	Resins (XAD),	LC/UV
Polyelectrolytes,		Charcoal, Ion-	LC
Carbohydrates,		exchangers or	LC
(different) HPC		special Adsor-	LC
Detergents (Anionics, Nonionics, Cationics)		bents	Special Methods/LC/TLC

Abbreviations to Annex A

GC = gas chromatography
LC = liquid chromatography
MS = mass spectrometry
HSD = halide specific detector
PID = photo ionization detector
FID = flame ionization detector
ECD = electron capture detector
NPD = nitrogen phosphorus detector
UV = ultraviolet detector
Fluor = fluorescence detector
EPA = Environmental Protection Agency
DIN = FRG-Standard
IR = infrared spectroscopy
HPC = high polymeric compounds
Electrochem = electrochemical detector

+) = method from author

ANNEX B

(to chapter VII)

Contents of lectures on modern chromatography (gas and liquid chromatography

1. Definition of chromatography and fundamentals of the chromatographic process
2. Possibilities of sampling and the different basic methods of chromatography
3. Properties and structures of the compact phase and from this derived fields of chromatography
4. Short review on history and present state and importance of chromatography
5. Forms of analytical and technical application
6. The theory of the chromatographic process and conclusions for practical work
7. How to make a chromatogram?
8. Preparation of columns for common GLC and LLC
9. Preparation of capillary columns for GC
10. Selection of liquid phases in GC
11. Polarity index and retention index
12. Detectors in gas chromatography, identification and quantification
    thermal conductivity detector
    flame ionization detector
    photo ionization detector
    thermo-ionic detector
    electron capture detector
    flame photometer detector
    microwave plasma detector
    coulometric and conductivity detectors
    mass spectrometer detector
13. Possibilities of sampling in capillary gas chromatography
14. Coupling of gas chromatography with enrichment procedures

15. Examples of application of gas chromatography in water analytics
16. The potential of high performance liquid chromatography (HPLC)
17. Modern equipment to HPLC
18. Examples of application of HPLC in water analytics