SUMMARY OF CONSIDERATIONS IN THE REPORT FROM THE OECD EXPERT GROUP ON PHYSICAL CHEMISTRY

Test Guidelines for Physical-Chemical Testing were prepared in draft form by the OECD Expert Group on Physical Chemistry (List of Participants appended). The drafts were issued in December 1979 from the Lead country (Germany) in a final report which included detailed considerations of the Group's approaches, objectives and general principles for physical-chemical testing, etc. The following text constitutes a summary of the considerations and is presented as background information to users of OECD Test Guidelines.

GENERAL

The Expert Group on Physical Chemistry decided early in its two year study that harmonizing the control of chemicals internationally requires the highest achievable degree of specificity in the technical instruments used for testing and evaluating chemicals, in particular when considering new chemicals.

After carefully selecting physical-chemical properties which appeared to be important, such as

- direct input parameters for hazard assessment (e.g. compartmentalisation: vapour pressure, water solubility, adsorption/desorption)
- prerequisites for performing other relevant tests (e.g. water solubility for testing abiotic and biotic degradation in water)
- guidance information for optimising other relevant tests (e.g. UV-VIS spectra for testing photodegradation),

this Group collected a large body of background material from national and international organisations.

The aim of the Expert Group was to elaborate the scientific-technical details of test methods for the determination of physical-chemical properties and their relation to degradation, mobility, accumulation and noxious effects.

For each of the physical-chemical properties which appeared to be important, a Test Guideline was developed containing descriptions of the methods to be used and guidelines for the evaluation of results. A series of reference substances was selected for the purpose of intercomparing and calibrating methods. In the future this selection of reference substances will provide a valuable basis for a better comparison of test results.

During the work of the Group, it was found that newly formulated Test Guidelines had to be drafted since the available standards, consensus methods or literature proposals did not completely satisfy the requirements under which this Group had to select methods – these had to apply to all or most new (hitherto unknown) substances.

The Group also identified eleven different tests which normally ought to be performed on the basic level (MPD) of testing and assessment of a new chemical.

USE OF PHYSICAL-CHEMICAL PROPERTIES IN ASSESSING THE POTENTIAL ENVIRONMENTAL HAZARD

Several human activities may result in chemicals being released into the environment, where they can initiate unwanted chemical and biological reactions.

The hazard which is posed by an environmental chemical can be given as a function of several factors, among which concentration and exposure depend in large part on physical-chemical properties of the chemical.

The concentration and exposure will depend upon a variety of input parameters. Prominent among these are:

- Release ("emission rate" into the environment)
- Mobility of the substance in the environment
- Degradation of substance in the environment (abiotic and biotic)
- Accumulation potential (biotic and abiotic).

In addition, other factors must be taken into consideration, such as mode of release into the environment, climatic/meteorological/geographical conditions, population densities (microbes, plants, animals, humans). Today, however, no reliable comprehensive environmental models are at hand. Thus a "worst possible case" estimate (the estimation of the worst possible environmental concentration) is often used to provide an upper limit in predictive environmental hazard evaluation.

Release

Estimates of the "emission rates" for a chemical product, at present, can only be crudely approximated from data on quantities marketed, its use and disposal patterns.

It is obvious, however, that knowledge of physical-chemical properties aids in estimating release probabilities, e.g. physical state, vapour pressure, water solubility, density, particle size, etc. These properties may allow prediction of the part(s) of the ecosystem which the substance can affect and, also, may indicate the form in which the substance may be.

Mobility

The mobility of a substance in the environment is defined as the ability of a substance to move within the environment. It is determined by the distribution behaviour of a substance between the environmental media (air, water, soil) and the transport behaviour within each medium. A knowledge of physical-chemical parameters such as

- vapour pressure curve
- water solubility
- adsorption/desorption
- volatility from aqueous solution
- complex formation ability
- density of liquids and solids
- particle size distribution
- viscosity of liquids
- surface tension of aqueous solutions,

allows an estimate of the distribution of a substance between air, water and soil, after its release into the environment. Thus, the knowledge of physical-chemical properties of a new substance (previously not described in the literature) is of major importance for a predictive hazard assessment.

Our knowledge of how physical-chemical properties can be used to predict compartmentalisation is still limited and only crude estimates can be obtained at the present time.

In principle it is possible to obtain an estimate of the distribution of a substance from a knowledge of physical-chemical parameters as long as accumulation effects are negligible and degradation in one or more of the compartments can be neglected (i.e. for persistent compounds). With a knowledge of the degradation rates in each medium, the behaviour of less persistent substances can also be estimated. However, progress in this field must await considerable advances in environment modelling and more reliable measurements of environmental degradation rates.

At present, even for the treatment of highly persistent compounds, only rough computations are feasible and a number of environmental models have been developed.

Mathematical models have already been used successfully to predict, within an order of magnitude, the distribution of chemical substances between air, water and soil.

Degradation/Accumulation

To obtain an estimate of environmental exposure, both the disappearance (degradation, mineralisation) and locality-specific accumulation of the substance need to be considered in addition to the estimated mobilities.

The Expert Group believed that some of the physical-chemical tests are well suited as "screening" tests for both degradation and, particularly, accumulation. It seems likely, for example, that a knowledge of the n-octanol/water partition coefficient could be used to predict the accumulation behaviour of a substance, whereas the hydrolysis behaviour is an important facet of degradation when in contact with water.

TEST GUIDELINES AND THEIR APPLICATION

In the development of Test Guidelines, the Group found that in no case could an existing test description be used directly in the form made available to the Group. But in several cases existing standards were sufficient as a basis for the development of the Guidelines.

The principal reason was frequently that existing test descriptions were not designed for all kinds of different (new) substances but rather for specific classes of chemicals, limited pressure ranges, etc.

Whilst the Test Guidelines represent the state-of-the-art, the OECD Expert Group on Physical Chemistry recommended that the OECD should seek ways to accomodate future progress in the development of improved and new methodology. In this conection it should be stressed, however, that proliferation of Test Guidelines is counter to harmonization. Therefore only such Test Guidelines should be selected which are demonstrably better (e.g. easier to perform, more precise, less costly) than existing ones or relate to a property for which a Test Guideline does not exist as yet.

Laboratory Intercomparison Studies

The Expert Group decided to subject a number of the newly designed Test Guidelines to laboratory intercomparison studies in order to ascertain their practicability and obtain information on cost.

In a Laboratory Intercomparison Programme, the following Guidelines were validated, partially in close co-operation with the Commission of the European Communities:

- Fat Solubility of Solid and Liquid Substances
- Water Solubility
- Vapour Pressure Curve
- Partition Coefficient (n-octanol/water)
- Viscosity of Liquids
- Density of Liquids and Solids
- Surface Tension of Aqueous Solutions
- Adsorption/Desorption, and
- Hydrolysis as a Function of pH.

The results of the Programme and the comments of the experts in the participating laboratories were carefully considered in developing the final versions of the Test Guidelines.

Prerequisites and Guidance Information

The Group defined prerequisites as information (normally derived from other tests) which must be known prior to properly applying the Test Guideline in the laboratory.

Guidance information, on the other hand, would be information which aids selection of the relevant test, performance of a test in the best possible way and interpretation of its results.

TABLE I

PHYSICAL-CHEMICAL PROPERTY	PREREQUISITES	GUIDANCE INFORMATION
UV-VIS Absorption Spectra		Molecular Formula, Structural Formula
Melting Point/ Melting Range		
Boiling Point/ Boiling Range		
Vapour Pressure Curve		Boiling + Melting Points, Relative Molecular Mass
Water Solubility	*	Structural Formula, Vapour Pressure Curve, Dissociation Constant, Hydrolysis (Preliminary)
Adsorption/Desorption	Water Solubility*	Boiling Point, Vapour Pressure Curve
Partition Coefficient (n-octanol/water)	Dissociation Constant, Water Solubility, Hydrolysis (Preliminary)*	
Complex Formation Ability	Water Solubility*, Dissociation Constant	Structural Formula
Density of Liquids and Solids		Boiling + Melting Points
Particle Size Distribution/Fibre Length and Diameter Distributions	Water Solubility, Information on fibrous nature of product and on stability of fibre shape under electron-microscopic conditions	Melting Point
Hydrolysis as a Function of pH	Water Solubility*	Vapour Pressure Curve
Dissociation Constants in Water	Water Solubility*	Structural Formula, Electric Conductivity
Screening Test for Thermal Stability and Stability in Air		Vapour Pressure Curve, Melting + Boiling Points, Structural Formula
Viscosity of Liquids	Density	Melting + Boiling Points
Surface Tension of Aqueous Solutions	Water Solubility	Structural Formula, Hydrolysis (Preliminary), Critical Micelle Concentration
Fat Solubility in Solid and Liquid Substances	*	Partition Coefficient, Water Solubility, Structural Formula, Vapour Pressure Curve, Stability at 50°C

* A suitable, specific analytical method must be available.

For the majority of Test Guidelines developed by the Group, prerequisites and guidance information have been identified, and they are summarised in Table I.

Purity of Substances

Virtually all substances of commercial relevance are placed on the market with production-related, and other, impurities (e.g. from raw materials). In some cases the impurities even exceed the substance itself by weight of by volume. In addition, some products of the chemical industry can only be placed on the market after addition of stabilisers.

With respect to performing physical-chemical tests, several impurity-related problems must be considered:

- Identification of substance: Since spectra structural formula, relative molecular mass, melting point, and boiling point are all part of the "identity-card" of a substance, they must be determined for the pure substance, otherwise literature will be cluttered with useless information.
- Sensitivity of tests in relation to impurities: Certain physical-chemical tests are inherently sensitive to the presence of particular types of impurities. Even a 1 per cent impurity level was estimated to have a major impact upon test results in a majority of cases considered by the Group.
- Potential impact of impurities upon the environment: Whenever a purified substance has been used in a physical-chemical test, the danger exists that environmentally relevant results of impurities may be overlooked (e.g. an impurity may be n-octanol soluble as opposed to the test substance in the partition coefficient determination).

ADDITIONAL REMARKS

Prediction of Physical Chemical-Properties from Structure

Experienced chemists are familiar with the concept of relating specific configurations of atoms within a molecule to the physical-chemical properties of that molecule (e.g. water solubility, vapour pressure, etc.). Equally, other scientists (biologists, toxicologists, etc.) make frequent use of qualitive structure-property relationships as "guidance information". In comparing biological activities of close chemical relatives of well-known substances, however, pronounced differences are not uncommonly observed.

In testing new chemicals, structure-property relations can be used as guidance information ("range finding") and then only with due caution. Virtually never can known structure-property relationships be considered sufficient as reasons not to perform any given test.

Considering existing (that is marketed) substances, structure-property relationships are among the most useful types of guidance information for selecting from among the great variety of substances which are likely to warrant thorough testing.

Reference Methods and Reference Substances

An important way to achieve reliable results, as well as compatibility and comparability of data with that from other laboratories, is through the use of reference materials. In the context of measurement compatibility, a reference material, in general, is considered to be any material, device, physical or chemicam system, for which definitive numerical values can be associated for specific properties and which can be used to calibrate a measurement process. In this sense, the reference material could be, for example, a chemical system that emits a substance which can be measured accurately and reproducibly, or a homogeneous stable metal alloy containing, for example, a known amount of chromium. It is through the use of reference materials that compatibility and harmonization in the field of analysing and testing chemicals can be most easily achieved.

This requires the appropriate combination of reference substances with reference test mehtods.

In collaboration with other Expert Groups of the OECD Chemicals Testing Programme, a list of calibration/comparison substances was drawn up.

The Group felt that it would be absolutely necessary for any laboratory using an individual test method to establish that it can measure correct values for the relevant reference substances or, alternatively, to explain systematic deviations. This procedure would also serve as an internal control in connection with good laboratory practice.

Agencies Providing Standards

ISO-Standards
International Organisation for Standardisation,
1, rue de Varembé, B.P. 56 CH-1211 Geneva, Switzerland

ASTM Standards
American Society for Testing and Materials,
1916, Race Street, Philadelphia, Pa. 19103-1187, U.S.A.

BSI Standards
British Standards Institution,
2 Park Street, London W1A 2BS, United Kingdom

DIN Standards
Deutsches Institut für Normung,
Burggrafenstr. 6, Postfach 1107 D-1000 Berlin, 30, Germany

JISC Standards
Japanese Industrial Standards Committee,
c/o Standards Department
Agency of Industrial Science and Technology, MITI
1-3-1, Kasumigaseki, Chiyoda-ku Tokyo 100, Japan

NF Standards
L'Association Française de Normalisation (AFNOR),
Tour Europe, Cedex 7, 92049 Courbevoie, France

PTB Method from:
Physikalisch-Technische Bundesanstalt,
Bundesallee 100, Postfach 3345 D-3300 Braunschweig, Germany

NEN Standards
Nederlands Normalisatie Instituut,
Kalfjeslaan 2, P.O. Box 5059 2600 GB, Delft, Netherlands

CEN Standards
European Committee for Standardization
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