

Recent reports

Recent reports published in *Pure and Applied Chemistry*

pH measurements in non-aqueous and mixed solvents: Predicting pH(PS) of potassium hydrogen phthalate for alcohol–water mixtures (Technical Report)

Synopsis: Predictive equations for estimating pH(PS) (PS = Primary Standard) of the potassium hydrogen phthalate buffer in any aqueous–alcoholic mixture are given as functions of the alcoholic moiety mole fraction, x , in the mixture and of the relative permittivity, ϵ , and the autoprotolysis constant, pK_{ap} , of the pure alco-

hol at 298.15 K. The two equations, one valid for 298.15 K and the other covering the 263–318 K temperature range, have been optimized by using the experimental data for pH(PS) in aqueous mixtures with the following alcohols: methanol, ethanol, propan-2-ol, ethane-1,2-diol, 2-methoxyethanol ('methylcellosolve'). The equations, tested on subsets generated from the full set by removing an entire co-solvent at a time, provide predicted pH(PS) values which differ from the 'true' ones by less than 0.1 pH over the entire range of co-solvent

composition: $0 < x \leq 0.75$. The predictive equations are recommended for calculating pH(PS) only in those aqueous–alcoholic media for which the corresponding experimental values are not available, and not as smoothing equations for water and its mixtures with the above-mentioned solvents.

This report was prepared for publication by: S. Rondinini, P.R. Mussini, T. Mussini and A. Vertova. Department of Physical Chemistry and Electrochemistry, University of Milan, Via Golgi 19, 20133 Milano, Italy. The full details are to be found in Pure Appl. Chem. 1998, 70(7), 1419–1422.

IUPAC Reports on Pesticides(40). Bound xenobiotic residues in food commodities of plant and animal origin (Technical Report)

Synopsis: In order to assess the dietary risk resulting from the use of pesticides or veterinary drugs, the nature of the chemical residues on food commodities needs to be determined. Elucidation of the nature of the chemical residue is carried out using radiolabelled studies, where the radiolabelled xenobiotic is applied or dosed in a manner which reflects its conditions of use. Food commodities are exhaustively extracted to remove the individual components of the residue. Once extracted, the identity and toxicological significance of the components can be assessed and, where appropriate, analytical methods developed to quantitatively determine the amount of the components in food items.

Depending on the characteristics of the components of the residue, the extraction regime may not remove all the chemical residue from the sample matrix. These residues are frequently characterized as being 'bound', however, the amount and nature of this residue will be highly dependent on the extraction regime used. To provide guidance and standardization, a definition of the term 'bound residues' is recommended. This definition builds on a previous IUPAC definition, but takes account of the current availability of enzyme systems, which effectively solubilize the entire matrix rather than extracting the residue. It is also recommended that where the extraction falls short of the full definition, then the residues should be termed as 'unextractable' and the conditions of the extraction should also be defined.

Where residues are bound, the assessment of dietary risk cannot be directly assessed, thus raising issues relating to the significance of the bound residue. The overall toxicological significance of a bound residue will depend primarily on its bioavailability and the level of exposure. In order to determine the bioavailability, study design is crucial in order to perform a critical safety assessment.

This report was prepared for publication by: M.W. Skidmore¹, G.D. Paulson², H.A. Kuiper³, B. Ohlin⁴ and S. Reynolds⁵. ¹Zeneca Agrochemicals, Jealotts Hill, Bracknell, UK. ²State Institute for Quality Control of Agricultural Products, Wageningen, Netherlands. ³US Department of Agriculture, ARS, Fargo, ND 58105, USA. ⁴National Food Administration, Uppsala, Sweden. ⁵Central Science Laboratories, York, UK. The full details are to be found in Pure Appl. Chem. 1998, 70(7), 1423–1447.

Critically evaluated propagation rate coefficients in free radical polymerizations—II. Alkyl methacrylates (Technical Report)

Synopsis: Propagation rate coefficients, k_p , with confidence ellipses of the Arrhenius parameters, are reported for bulk free-radical homopolymerizations of *n*-butyl and *n*-dodecyl methacrylate at ambient pressure and low conversion. The data, which are from independent experiments in two laboratories, were obtained by the pulsed-laser polymerization/size-exclusion chromatography method. They obey the consistency criteria established for this technique. Plotting the *n*-butyl and *n*-dodecyl methacrylate k_p data, together with the benchmark k_p values for methyl methacrylate and recent data for four other linear and branched alkyl methacrylates, clearly shows a pronounced family type behaviour of alkyl methacrylate k_p .

This report was prepared for publication by: Sabine Beuermann and Michael Buback. Institut für Physikalische Chemie der Universität Göttingen, Tammannstr. 6, D-37077 Göttingen, Germany. The full details are to be found in Pure & Appl. Chem. 1998, 70(7), 1415–1418.

Spectroelectrochemistry. A survey of *in situ* spectroscopic techniques (Technical Report)

Synopsis: In this technical paper a summary of the available *in situ* spectroelectrochemical methods, their basic principles, their typical applications, and their limitations is given. With respect to the names of the methods and usual abbreviations, the paper follows the literature as far as possible, but tries to point out inconsistencies. An introductory section gives a summary of the basic equations and introduces the IUPAC recommendations for quantities and symbols.

This report was prepared for publication by: W. Plieth¹, G.S. Wilson² and C. Gutiérrez de la Fe³. ¹Institut für Physikalische Chemie und Elektrochemie, Technische Universität Dresden, Bergstr. 66b, D-01062 Dresden, Germany. ²Department of Chemistry, University of

Kansas, Lawrence, KS 66045, USA. ³Instituto de Quimica Fisica 'Rocasolano', Calle Serrano 119, Madrid 28006, Spain. The full details are to be found in Pure Appl. Chem. 1998, **70**(7), 1395–1414.

Analytical aspects of chemically modified electrodes: classification, critical evaluation and recommendations (IUPAC Recommendations 1998)

Synopsis: Analytical aspects of chemically modified electrodes (CMEs) are critically reviewed. Effects of analyte and/or reagent accumulation, chemical transformation, electrocatalysis, permeability, ionic equilibria, controlled release and change of mass, as well as combinations of these effects are evaluated and classified. In addition, relevant definitions are provided and recommendations formulated for the most effective CME operation.

*This report was prepared for publication by: Wlodzimierz Kutner¹, Joseph Wang,² Maurice L'her,³ and Richard P. Buck⁴. ¹Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44, 01-224 Warsaw, Poland. ²Department of Chemistry and Biochemistry, New Mexico State University, Las Cruces, NM 88003, USA. ³Faculté des Sciences et Techniques, URA CNRS 322, 6 avenue V. Le Gorgeu, B.P. 809-29285, Brest Cedex, France. ⁴Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, USA. The full details are to be found in Pure Appl. Chem. 1998, **70**(6), 1301–1318*

Glossary of terms used in medicinal chemistry (IUPAC Recommendations 1998)

Synopsis: The objective of this glossary is to provide, in a single document, a consistent terminology and concise definitions of terms covering the various aspects of medicinal chemistry. This was felt necessary with regard to the rapid changes occurring in medicinal chemistry and also by the need to establish international definition standards. Effectively the possibility exists that in different countries certain terms may not have the same meaning, in such a case the creation of an internationally accepted definition is particularly justified.

A Working Party belonging to the IUPAC Section on Medicinal Chemistry has therefore been assembled which prepared the present glossary. Concise but sufficiently explanatory definitions have been formulated for about one hundred commonly employed terms which can be considered of particular interest to the medicinal chemistry community. The glossary has been compiled in part from definitions proposed by the Working Party,

in part from earlier IUPAC glossaries, and in part from well-accepted definitions taken from the literature but which were sometimes published in journals or books that may not be readily accessible.

*This report was prepared for publication by: C.G. Wermuth¹, C.R. Ganellin², P. Lindberg³ and L.A. Mitscher⁴. ¹Faculté de Pharmacie, Université Louis Pasteur, Strasbourg, France. ²University College London, London, UK. ³Astra Hässle AB, Mölndal, Sweden. ⁴School of Pharmacy, University of Kansas, Lawrence, Kansas, USA. The full details are to be found in Pure Appl. Chem. 1998, **70**(5), 1129–1143.*

Guidelines for presentation of methodological choices in the publication of computational results. A. *Ab initio* electronic structure calculations (IUPAC Recommendations)

Synopsis: Guidelines are presented to assist authors in preparing manuscripts that describe the results of *ab initio* computation. These guidelines are not intended to recommend how *ab initio* calculations should be done, but rather to ensure that the reader can have a clear understanding of what was actually carried out. They are written in a form to facilitate reprinting in original research journals and as information sheets that can be distributed to authors and reviewers.

*This report was prepared for publication by: James E. Boggs, Department of Chemistry, The University of Texas, Austin, Texas 78712, USA. The full details are to be found in Pure Appl. Chem. 1998, **70**(4), 1015–1018.*

Guidelines for calibration in analytical chemistry—Part 1: Fundamentals and single component calibration (IUPAC Recommendations 1998)

Synopsis: This IUPAC nomenclature document has been prepared to establish a uniform and meaningful approach to terminology, notation and formulation for calibration in analytical chemistry. In this first part, the general fundamentals of calibration are presented, namely for both relationships of qualitative and quantitative variables (relations between variables characterizing certain types of analytes and measured signals in certain positions of a measured function on the one hand and between variables characterizing the amount or concentration of the chemical species and the intensities of the measured signals, on the other hand). On this basis, the fundamentals of the common single component calibration which models the relationships

$y = f(x)$ between the signal intensities y and the amounts or concentration are represented. Additional papers will be prepared dealing with extensive relationships between several signal intensities and analyte contents, namely with multivariate calibration and with optimization and experimental design.

This report was prepared for publication by: K. Danzer and L. A. Currie, The full details are to be found in Pure Appl. Chem. 1998, 70(4), 993–1014.

Definitions of terms relating to the non-ultimate mechanical properties of polymers (IUPAC Recommendations 1998)

Synopsis: The document gives definitions of terms related to the nonultimate mechanical behaviour of polymeric materials, in particular bulk polymers and concentrated solutions and their elastic and viscoelastic properties. The terms which have been selected are those met in the conventional mechanical characterization of isotropic polymeric materials. They have additionally been limited to those which can be defined precisely and with mathematical rigour. They are arranged in sections dealing with basic definitions of stress and strain, deformations used experimentally, stresses observed experimentally, quantities relating stress and deformation, linear viscoelastic behaviour and oscillatory deformations and stresses used experimentally for solids. An index, an alphabetical list of terms and a glossary of symbols are included for ease of reference.

This report was prepared for publication by: A. Kaye (UK), R.F.T. Stepto (UK), W. J. Work (USA), J. V. Alemán (Spain), A. Ya. Malkin (Russia). The full details are to be found in Pure Appl. Chem. 1998, 70(3), 701–754.

Nomenclature, symbols, units and their usage in spectrochemical analysis—XIV. Laser-based atomic spectroscopy: Proposal for a new notation (IUPAC Recommendations 1998)

Synopsis: This report is the 14th in a series on Spectrochemical Methods of Analysis issued by IUPAC Commission V.4. Because of the complexity and the lack of uniformity of the present nomenclature (e.g. '2 step excited resonance fluorescence', 'resonance enhanced multiphoton ionization', etc.) a new way is needed to describe these transitions. The aim of this document is therefore to present a new notation, the IUPAC Notation, to describe the various processes involved in atomic laser spectroscopy. Using a few assumptions,

this notation has the advantage of being simple and systematic. States and processes can be described in a general way irrespective of the type of laser spectrometry.

This report was prepared for publication by: N. Omenetto,¹ J.-M. Mermet,² G.C. Turk,³ and D. S. Moore⁴.¹Joint Research Centre, Ispra Establishment, I-21020 Ispra (Varese), Italy. ²Department of Spectroscopic Analysis, Université de Lyons, Lyons, France. ³Inorganic Analytical Research Division, NIST, Gaithersburg, MD 20899, USA. ⁴Chemical Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM 87544, USA. The full details are to be found in Pure Appl. Chem. 1998, 70(2), 517–526.

History of the recommended atomic-weight values from 1882 to 1997: A comparison of differences from current values to the estimated uncertainties of earlier values (Technical Report)

Synopsis: International commissions and national committees for atomic weights (mean relative atomic masses) have recommended regularly updated, best values for these atomic weights as applicable to terrestrial sources of the chemical elements. Presented here is a historically complete listing starting with the values in F.W. Clarke's 1882 recalculation, followed by the recommended values in the annual reports of the American Chemical Society's Atomic Weights Commission. From 1903, an International Commission published such reports and its values (scaled to an atomic weight of 16 for oxygen) are used here in preference to those of national committees of the UK, Germany, Spain, Switzerland and the USA. We have, however, made scaling adjustments from Ar(¹⁶O) to Ar(¹²C) where not negligible.

From 1920, this International Commission constituted itself under the International Union of Pure and Applied Chemistry (IUPAC). Since then, IUPAC has published reports (mostly biennially) listing the recommended atomic weights, which are reproduced here. Since 1979, these values have been called the 'standard atomic weights' and, since 1969, all values have been published with their estimated uncertainties. Few of the earlier values were published with uncertainties. Nevertheless, we assessed such uncertainties on the basis of our understanding of the likely contemporary judgement of the values' reliability. While neglecting remaining uncertainties of 1997 values, we derive 'differences' and a retrospective index of reliability of atomic-weight values in relation to assessments of uncertainties at the time of their publication. A striking improvement in reliability appears to have been achieved since the commissions have imposed upon themselves the rule of recording

estimated uncertainties from all recognized sources of error.

This report was prepared for publication by: T. B. Coplen and H. S. Peiser, U.S. Geological Survey, 431 National Center, Reston, VA 20192, USA. The full details are to be found in Pure Appl. Chem. 1998, 70(1), 237–257.

Isotopic compositions of the elements 1997 (Technical Report)

Synopsis: The Commission's Subcommittee for the Isotopic Composition of the Elements (SIAM) has carried out its biennial review of isotopic compositions, as determined by mass spectrometry and other relevant methods. This involves a critical evaluation of the published literature, element by element, and forms the basis of the table of isotopic compositions of the elements as determined by mass spectrometry presented here. New guidelines have been used to arrive at the uncertainties on the isotopic abundances and there are numerous changes to the table since it was last published in 1991. Atomic weights calculated from this table are consistent with Ar(E) values listed in the *Table of Standard Atomic Weights 1997*.

This report was prepared for publication by: K.J.R. Rosman¹ and P.D.P. Taylor². ¹Department of Applied Physics, Curtin University of Technology, GPO Box U1987, Perth 6001, Australia. ²Institute for Reference Materials and Measurements, European Commission-JRC, B-2440 Geel, Belgium. The full details are to be found in Pure Appl. Chem. 1998, 70(1), 217–235.

Nomenclature of fused and bridged fused ring systems (IUPAC Recommendations)

Synopsis: These recommendations constitute a comprehensive documentation for naming fused ring systems and bridged fused ring systems. It expands and extends the recommendations given in rules A-21, A-22, A-23, A-34, B-3 of the IUPAC Nomenclature of Organic Chemistry, Sections A, B, C, D, E, F and H, 1979 and rule R-2.4.1 of A Guide to IUPAC Nomenclature of Organic Compounds, 1993. Any ring system with two or more rings ortho- or ortho- and peri-fused together may be named by these recommendations. Two rings which are ortho-fused together have only two atoms and one bond in common. The nomenclature of spiro systems and von Baeyer nomenclature will be considered in separate recommendations.

This report was prepared for publication by: G.P. Moss. Department of Chemistry, Queen Mary and Westfield

College, Mile End Road, London, E1 4NS, UK. The full details are to be found in Pure Appl. Chem. 1998, 70(1), 143–216.

Recommendations for the presentation of NMR structures of proteins and nucleic acids (IUPAC Recommendations 1998)

Synopsis: The recommendations presented here are designed to support the easier communication of NMR data and NMR structures of proteins and nucleic acids through unified nomenclature and reporting standards. Much of this document pertains to the reporting of data in journal articles; however, in the interest of the future development of structural biology, it is desirable that the bulk of the reported information be stored in computer-accessible form and be freely accessible to the scientific community in standardized formats for data exchange. These recommendations stem from an IUPAC-IUBMB-IUPAB interunion venture with the direct involvement of ICSU and CODATA. The Task Group has reviewed previous formal recommendations and has extended them in the light of more recent developments in the field of biomolecular NMR spectroscopy. Drafts of the recommendations presented here have been examined critically by more than 50 specialists in the field and have gone through two rounds of extensive modification to incorporate suggestions and criticisms.

This report was prepared for publication by: John L. Markley¹, Ad Bax², Yoji Arata³, C.W. Hilbers⁴, Robert Kaptein⁵, Brian D. Sykes⁶, Peter E. Wright⁷ and Kurt Wüthrich⁸. ¹Department of Biochemistry, University of Wisconsin-Madison, Madison, WI, USA. ²Laboratory of Chemical Physics, NIDDK, National Institutes of Health, Bethesda, MD, USA. ³Water Research Institute, Tsukuba, Japan. ⁴Laboratory of Biophysical Chemistry, University of Nijmegen, the Netherlands. ⁵Department of Chemistry, University of Utrecht, the Netherlands. ⁶Department of Biochemistry, University of Alberta, Edmonton, Alberta, Canada. ⁷Department of Molecular Biology, The Scripps Research Institute, La Jolla, CA, USA. ⁸Institut für Molekularbiologie und Biophysik, ETH Hönggerberg, Zürich, Switzerland (convenor of the task group to whom correspondence should be addressed). The full details are to be found in Pure Appl. Chem. 1998, 70(1), 117–142.