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UDK 541.121:519.24

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К ВОПРОСУ О ТОЧНОСТИ ОПРЕДЕЛЕНИЯ pK_a ПОТЕНЦИОМЕТРИЧЕСКИМ И СПЕКТРОФОТОМЕТРИЧЕСКИМ МЕТОДАМИ

В настоящей работе рассмотрено влияние инструментальной погрешности потенциометрического (рН-метрического) и спектрофотометрического методов на величину константы протонического равновесия pK_a и возможность достоверной оценки экспериментально найденных значений этой константы. Выбор метода исследования и планирование условий эксперимента, позволяющего наиболее точно определить величину pK_a , тесно связаны с предварительной оценкой влияния этой погрешности.

Стенка влияния абсолютных погрешностей прямых измерений рН и систематических растворов на абсолютную погрешность результата косвенных измерений зависит от вида аналитической функции, лежащей в основе расчета pK_a [1].

В качестве модельного соединения для оценки pK_a и σ_{pK_a} потенциометрически и спектрофотометрически методами нами выбран 1-метилпиперазинский бензимидазола — катионобразующий лиганд, проявляющий амфотерные свойства [2]. Исследовано равновесие протонирования молекулярной формы лиганда: $H^+H^+ \rightleftharpoons HH^+$.

ЭКСПЕРИМЕНТАЛЬНАЯ ЧАСТЬ

Потенциометрическое титрование 0,1 и 0,2 ммоль 1-метилпиперазинского бензимидазола, предварительно переведенного хлорсероводородной кислотой в протонированную форму, проводили 0,1 М раствором NaOH на рН-метре рН-121 со стеклянным индикаторным электродом ($\alpha=0,1$, NaCl).

Электронные спектры 1-метилпиперазинского бензимидазола в растворах с различным значением рН записаны на регистрирующем спектрофотометре Спектрд в кюветках с $l=1,0$ см ($c_L=3,5 \cdot 10^{-4}$ М).

РЕЗУЛЬТАТЫ И ИХ ОБСУЖДЕНИЕ

При потенциометрическом титровании щелочью слабой кислоты или предварительное протонированного основания расчет pK_a (с учетом уравнения электронейтральности и материального баланса частиц) проводят по формуле [3, 4]

$$pK_a = pH + \lg \frac{(1-\alpha) c_L - [H^+] + [OH^-]}{\alpha c_L + [H^+] - [OH^-]}, \quad (1)$$

где c_L — аналитическая концентрация лиганда, α — степень нейтрализации лиганда. После дифференцирования уравнения (1) как функции pK_a от рН получено [4] выражение для расчета значений абсолютного стандартного отклонения, характеризующего погрешность измерения pK_a по уравнению (1), поскольку известно значение стандартного отклонения σ_{pH} , характеризующего погрешность измерения рН

$$\sigma_{pK_a}^2 = \sigma_{pH}^2 \left(1 + \frac{c_L ([H^+] + [OH^-])}{c_L (1-\alpha) - [H^+] + [OH^-]} \{ \alpha c_L + [H^+] - [OH^-] \}^2 \right). \quad (2)$$

На рис. 1 представлены кривые $\sigma_{pK_a} = f(pH)$, рассчитанные при использованных нами рабочих концентрациях лиганда $4 \cdot 10^{-4}$ и $8 \cdot 10^{-4}$ М, а также при концентрациях

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Spectrophotometric Determination of Trace Amounts of Copper in Tungsten Metal Powder Andrew S.

Prokopovitch, T. E. Green, 1961 *CRC Handbook of Chemistry and Physics* William M. Haynes, 2016-06-22 Proudly serving the scientific community for over a century this 97th edition of the CRC Handbook of Chemistry and Physics is an update of a classic reference mirroring the growth and direction of science This venerable work continues to be the most accessed and respected scientific reference in the world An authoritative resource consisting of tables of data and current international recommendations on nomenclature symbols and units its usefulness spans not only the physical sciences but also related areas of biology geology and environmental science The 97th edition of the Handbook includes 20 new or updated tables along with other updates and expansions It is now also available as an eBook This reference puts physical property data and mathematical formulas used in labs and classrooms every day within easy reach **CRC Handbook of Basic Tables for**

Chemical Analysis Thomas J. Bruno, Paris D.N. Svoronos, 2020-07-30 Researchers in chemistry chemical engineering pharmaceutical science forensics and environmental science make routine use of chemical analysis but the information these researchers need is often scattered in different sources and difficult to access The CRC Handbook of Basic Tables for Chemical Analysis Data Driven Methods and Interpretation Fourth Edition is a one stop reference that presents updated data in a handy format specifically designed for use when reaching a decision point in designing an analysis or interpreting results This new edition offers expanded coverage of calibration and uncertainty and continues to include the critical information scientists rely on to perform accurate analysis Enhancements to the Fourth Edition Compiles a huge array of useful and important data into a single convenient source Explanatory text provides context for data and guidelines on applications Coalesces information from several different fields Provides information on the most useful wet chemistry methods as well as instrumental techniques with an expanded discussion of laboratory safety Contains information of historical importance necessary to interpret the literature and understand current methodology Unmatched in its coverage of the range of information scientists need in the lab this resource will be referred to again and again by practitioners who need quick easy access to the data that forms the basis for experimentation and analysis **Surfactant-based Sensors in Chemical and**

Biochemical Detection J G Manjunatha, 2023-10-11 Describing the importance of surfactants in electrochemical investigations related to biologically and environmentally vital chemicals this book charts the progression of highly responsive electrochemical sensors using surfactants as a modifying agent in the sensor field It provides contributed chapters from respected researchers on information concerning the activity of target molecules and electron transfer kinetics arising at the surface of the fabricated sensor materials Surfactant based electrochemical sensors are of great interest in the quest to find low cost fast and highly responsive sensing devices and one aim of this book is to help improve the competence and knowledge in this newly emerging interdisciplinary research area Attracting an audience of students academics

industrialists and engineers it will interest researchers seeking to use non toxic sensors in their detection challenges

Spectrophotometric Determination of the PKa's of Some Aromatic Amines Mark Bixler,1963 The dissociation constants of the conjugate acids of aniline alpha naphthylamine and beta naphthylamine have been determined from their ultraviolet absorption spectra in 50% by weight ethanol water solution The values obtained have been compared with potentiometric measurements

Analytical Chemistry Gary D. Christian,Purnendu K. Dasgupta,Kevin A. Schug,2013-10-07 With the 7th Edition of Analytical Chemistry renowned chemists Purnendu Sandy Dasgupta and Kevin Schug both of the University of Texas Arlington join the author team The new edition focuses on more in depth coverage of the principles and techniques of quantitative analysis and instrumental analysis aka Analytical Chemistry The goal of the text is to provide a foundation of the analytical process tools and computational methods and resources and to illustrate with problems that bring realism to the practice and importance of analytical chemistry It is designed for undergraduate college students majoring in chemistry and in fields related to chemistry

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Master Analytical Manual Oak Ridge National Laboratory. Analytical Chemistry Division,1958

Scientific and Technical Aerospace Reports ,1965 Lists citations with abstracts for aerospace related reports obtained from world wide sources and announces documents that have recently been entered into the NASA Scientific and Technical Information Database

Physicochemical and Biomimetic Properties in Drug Discovery Klara Valko,2013-11-25

Demonstrating how and why to measure physicochemical and biomimetic properties in early stages of drug discovery for lead optimization Physicochemical and Biomimetic Properties in Drug Discovery encourages readers to discover relationships between various measurements and develop a sense of interdisciplinary thinking that will add to new research in drug

discovery This practical guide includes detailed descriptions of state of the art chromatographic techniques and uses real life examples and models to help medicinal chemists and scientists and advanced graduate students apply measurement data for optimal drug discovery *Prof. of Drug Substances, Excipients and Related Methodology* Abdulrahman Al-Majed, 2021-01-16

Profiles of Drug Substances Excipients and Related Methodology Volume 46 contains comprehensive profiles of five drug compounds Darunavir Bisoprolol Betaxolol Rabeprazole and Irbesartan In addition the work contains a chapter reviewing Bioassay Methods and Their Applications in Herbal Drug Research The comprehensive reviews in the book cover all aspects of drug development and the formulation of drugs helping readers understand how the drug development community remains essential to all phases of pharmaceutical development In addition this work answers why such profiles are of immeasurable importance to workers in the field The scope of the Profiles series encompasses review articles and database compilations that fall within one or more of the following five broad categories Physical Profiles of Drug Substances and Excipients Analytical Profiles of Drug Substances and Excipients ADME Profiles of Drug Substances and Excipients Methodology Related to the Characterization of Drug Substances and Excipients and Methods of Chemical Synthesis Contains contributions from leading authorities Presents an excellent overview on the physical chemical and biomedical properties of some regularly prescribed drugs Includes a cumulative index in each volume **Indexes to the Oak Ridge National Laboratory Master Analytical Manual** Oak Ridge National Laboratory, 1963 **Cumulated Index Medicus**, 1968 **Profiles of Drug Substances, Excipients and Related Methodology** Harry G. Brittain, 2007-11-14 Whilst following in the footsteps of previous volumes by presenting comprehensive reviews of drug substances and additional materials this title also heralds a significant expansion of the scope of the series Traditional contributions will now also be augmented by publication of critical review chapters that summarize information related to the characterization of drug substances and excipients This change is required to better meet the needs of the pharmaceutical community and to allow the development of a timely vehicle for publishing review materials on this topic The scope of the Profiles series will encompass review articles and database compilations that fall within one of the following six broad categories Physical profiles of drug substances and excipients Analytical profiles of drug substances and excipients Drug metabolism and pharmacokinetic profiles of drug substances and excipients Methodology related to the characterization of drug substances and excipients Methods of chemical synthesis and Reviews of the uses and applications for individual drug substances classes of drug substances or excipients Presents comprehensive reviews covering all aspects of drug development and formulation of drugs Now encompassing critical review chapters Meets the information needs of the drug development community

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Table of Contents Potentiometric And Spectrophotometric Determination Of The

1. Understanding the eBook Potentiometric And Spectrophotometric Determination Of The
 - The Rise of Digital Reading Potentiometric And Spectrophotometric Determination Of The
 - Advantages of eBooks Over Traditional Books
2. Identifying Potentiometric And Spectrophotometric Determination Of The
 - Exploring Different Genres
 - Considering Fiction vs. Non-Fiction
 - Determining Your Reading Goals
3. Choosing the Right eBook Platform
 - Popular eBook Platforms
 - Features to Look for in an Potentiometric And Spectrophotometric Determination Of The
 - User-Friendly Interface
4. Exploring eBook Recommendations from Potentiometric And Spectrophotometric Determination Of The
 - Personalized Recommendations
 - Potentiometric And Spectrophotometric Determination Of The User Reviews and Ratings
 - Potentiometric And Spectrophotometric Determination Of The and Bestseller Lists
5. Accessing Potentiometric And Spectrophotometric Determination Of The Free and Paid eBooks
 - Potentiometric And Spectrophotometric Determination Of The Public Domain eBooks
 - Potentiometric And Spectrophotometric Determination Of The eBook Subscription Services
 - Potentiometric And Spectrophotometric Determination Of The Budget-Friendly Options

6. Navigating Potentiometric And Spectrophotometric Determination Of The eBook Formats
 - ePub, PDF, MOBI, and More
 - Potentiometric And Spectrophotometric Determination Of The Compatibility with Devices
 - Potentiometric And Spectrophotometric Determination Of The Enhanced eBook Features
7. Enhancing Your Reading Experience
 - Adjustable Fonts and Text Sizes of Potentiometric And Spectrophotometric Determination Of The
 - Highlighting and Note-Taking Potentiometric And Spectrophotometric Determination Of The
 - Interactive Elements Potentiometric And Spectrophotometric Determination Of The
8. Staying Engaged with Potentiometric And Spectrophotometric Determination Of The
 - Joining Online Reading Communities
 - Participating in Virtual Book Clubs
 - Following Authors and Publishers Potentiometric And Spectrophotometric Determination Of The
9. Balancing eBooks and Physical Books Potentiometric And Spectrophotometric Determination Of The
 - Benefits of a Digital Library
 - Creating a Diverse Reading Collection Potentiometric And Spectrophotometric Determination Of The
10. Overcoming Reading Challenges
 - Dealing with Digital Eye Strain
 - Minimizing Distractions
 - Managing Screen Time
11. Cultivating a Reading Routine Potentiometric And Spectrophotometric Determination Of The
 - Setting Reading Goals Potentiometric And Spectrophotometric Determination Of The
 - Carving Out Dedicated Reading Time
12. Sourcing Reliable Information of Potentiometric And Spectrophotometric Determination Of The
 - Fact-Checking eBook Content of Potentiometric And Spectrophotometric Determination Of The
 - Distinguishing Credible Sources
13. Promoting Lifelong Learning
 - Utilizing eBooks for Skill Development
 - Exploring Educational eBooks
14. Embracing eBook Trends
 - Integration of Multimedia Elements

- Interactive and Gamified eBooks

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