

高等学校教材

# Analytical Chemistry

# 分析化学 (双语版)

魏云霞 马明广 编



化学工业出版社

013069932

065-43

38

英表計代國華是，新辭科文的華譯版以新重要器工量測華譯科本對華學高干

此以能應取以的取而可能能強到定的學城取合

並局，31個面局，第一本基林地華出誰位工外，華出對華學高由國已容內圖解，第21共計全

製不枚章註第，性民，容內學以漸心將，以漸細細，漸平細細，以總得公以漸，照以的漸選突已

本版介，“最小章本”備以備文中皆寫世以章第，區華主華干期以，容以面全了計選港代以漸第

$\text{HPO}_3 + \text{H}_2\text{O} + \text{H}^+ \rightleftharpoons \text{H}_2\text{P}_2\text{O}_7 + \text{H}^+$  高等學校教材

高的應則漸效華出得代其有合以應得，以應的漸則華出得代其有合以應得，以應的漸則華出得代其有合以應得

的并工等以得代其有合以應得，以應的漸則華出得代其有合以應得，以應的漸則華出得代其有合以應得

# Analytical Chemistry

## 分析化学

(双语版)

魏云霞 马明广 编



$\text{H}_2\text{PO}_4^- + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_4\text{P}_2\text{O}_7 + \text{H}_2\text{O}$

$\text{Sn}^{4+} + 2\text{H}_2\text{O} + 4\text{e}^- \rightleftharpoons \text{Sn} + 4\text{OH}^-$

$\text{Sn}^{4+} + 2\text{e}^- \rightleftharpoons \text{Sn}^{2+}$

$\text{Bi}^{3+} + 3\text{e}^- \rightleftharpoons \text{Bi}$

$\text{K}^+ + \text{e}^- \rightleftharpoons \text{K}$

$\text{Li}^+ + \text{e}^- \rightleftharpoons \text{Li}$

①  $E^\ominus$  for  $\text{Br}_2/\text{Br}^-$  is used for reactions of  $\text{Br}_2$  while  $E^\ominus$  for  $\text{Br}_2/\text{aq}$  is used for reactions of  $\text{Br}_2$  in aqueous solution.

②  $E^\ominus$  for  $\text{I}_2/\text{I}^-$  is used for reactions of  $\text{I}_2$  while  $E^\ominus$  for  $\text{I}_2/\text{aq}$  is used for reactions of  $\text{I}_2$  in aqueous solution.

(110001) 中国标准书号 7-113-01000-1 化学工业出版社

187mm×125mm 1/16 印张 9.2 字数 230 千字 2013年10月北京第1次印刷



化学工业出版社

· 北京 ·

定价：28.00元

定价：28.00元



北航

C1677975

065-43

38

013069335

本书是根据教育部关于高等学校本科教学质量工程要重视双语教学的文件精神,参考国外优秀英文原版分析化学教材,结合双语教学的实践经验编写而成的双语教材。

全书共 12 章,涵盖内容与国内高等学校化学、化工类分析化学教材基本一致,包括绪论,误差与实验数据的处理,滴定分析总论,酸碱平衡,酸碱滴定,络合滴定等内容。另外,第 12 章对环境污染物的分析进行了全面的介绍。为便于学生学习,每章后均设有中文撰写的“本章小结”,介绍本章的基本要求、基本概念、主要计算公式等内容。

本书可作为高等院校化学、化工专业分析化学课程的教材,特别适合开设分析化学双语课程的高等院校,亦可供理、工、农高等院校的相关专业作为教材或教学参考书,也可供从事分析化学工作的科技人员阅读和参考。

#### 图书在版编目(CIP)数据

分析化学(双语版)/魏云霞,马明广编. —北京:  
化学工业出版社, 2013. 8  
高等学校教材  
ISBN 978-7-122-18047-6

I. ①分… II. ①魏… ②马… III. ①分析化学-  
高等学校-教材-汉、英 IV. ①065

中国版本图书馆 CIP 数据核字 (2013) 第 171453 号

责任编辑: 窦 臻  
责任校对: 蒋 宇

文字编辑: 刘志茹  
装帧设计: 王晓宇

出版发行: 化学工业出版社(北京市东城区青年湖南街 13 号 邮政编码 100011)

印 装: 三河市延风装订厂

787mm×1092mm 1/16 印张 9 1/4 字数 230 千字 2013 年 10 月北京第 1 版第 1 次印刷

购书咨询: 010-64518888 (传真: 010-64519686) 售后服务: 010-64518899

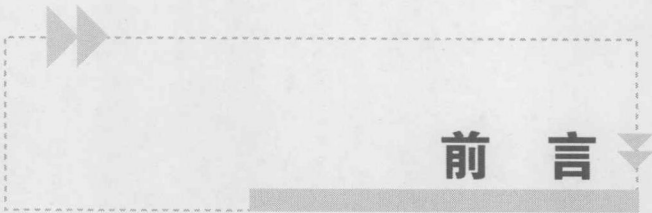
网 址: <http://www.cip.com.cn>

凡购买本书,如有缺损质量问题,本社销售中心负责调换。

定 价: 25.00 元

版权所有 违者必究





# 前言

## FOREWORD

分析化学是高等院校化学专业的一门基础课程,同时,分析化学具有很强的实用性,是理论与实际密切结合的学科,对于学生树立准确的量的概念,培养严谨的科学态度等方面发挥着重要作用。

在教育部关于高等学校本科教学质量工程要重视双语教学的文件精神传达后,许多高等院校都为化学专业高年级本科生开设了分析化学双语课。目前,双语教学模式与其他教学模式的区别主要体现在教材选取和授课方式两个方面。教材选取上,或直接采用英文原版教材,或采用中文版教材配套英文讲义;授课方式上,有的采用全英文授课,有的在使用原版英文教材的基础上全中文授课。

原版教材内容体系比较庞大,与国内教学要求难以完全符合,如果采用中文版教材,再配以英文补充材料,则双语教学体现得不够充分,效果不明显。鉴于此,我们根据分析化学教学大纲的要求,在总结多年分析化学双语教学工作经验的基础上,参考多种相关教材编撰了这本双语教材,以满足高等院校分析化学双语教学的需要。

本教材在内容的安排上参照了《分析化学》(第四版,华中师范大学、东北师范大学等六校合编)中文教材,将众多化学分析方法按大类编写,以定量分析方法为主,突出理科特点,在符合发展趋势的同时重视学习的规律性和逻辑性。英文内容参考多种国外原版教材,力求语言表述精准。

本教材由魏云霞(第1章,第3~8章)、马明广(第2章,第9~12章,附录)共同编写,全书经多次认真研究讨论、反复修改后定稿。本教材的编写,参考了国内外相关分析化学教学参考书,在本书的文献部分已经列出,在此对这些参考书的作者表示感谢。同时,本教材的编写得到了兰州城市学院教务处、化学与环境科学学院赵国虎院长及招生就业处李生英处长的大力支持,在此一并表示感谢!

分析化学双语教学作为一种高校教学改革的尝试,内容还有待完善,不妥和疏漏之处在所难免,恳切希望使用本书的师生们提出宝贵建议。

编者

2013年4月

# 目 录

## CONTENTS

### Chapter 01 Introduction

1.1 What is analytical chemistry .....	1
1.2 Measurement of the analyte .....	2
1.3 Range .....	2
1.4 The analytical perspective .....	3

### Chapter 02 Errors and Data Treatment in Quantitative Analysis

2.1 Determinate errors .....	5
2.2 Indeterminate errors .....	6
2.3 Accuracy and precision .....	6
2.3.1 Ways of expressing accuracy .....	7
2.3.2 Ways of expressing precision .....	8
2.4 The distribution of measurements and results .....	9
2.4.1 Populations and samples .....	10
2.4.2 Probability distributions for populations .....	10
2.4.3 Confidence intervals for populations .....	11
2.4.4 Probability distributions for samples .....	12
2.5 Confidence intervals for samples .....	14
2.6 Rejection of a result .....	15
2.7 Significant figures .....	16
2.7.1 Multiplication and division .....	17
2.7.2 Addition and subtraction .....	18
2.7.3 Logarithms .....	19
2.8 Rounding off .....	19
本章小结 .....	20
PROBLEMS .....	21

## Chapter 03

## Chapter 03 Titrimetric Analysis

3.1 General principles .....	23
3.1.1 Titration .....	23
3.1.2 Standard solutions .....	23
3.1.3 Classification of volumetric methods .....	24
3.2 Titer .....	25
本章小结 .....	26

## Chapter 04

## Chapter 04 Acid-Base Equilibria

4.1 Aqueous Acid-Base Theories .....	27
4.2 Acid-Base Equilibria in Water .....	28
4.3 The pH Scale .....	29
4.3.1 Proton Balance Equation .....	30
4.3.2 Weak Acids and Bases .....	30
4.3.3 Salts of Weak Acids and Bases .....	31
4.3.4 Polyprotic Acids and Their Salts .....	32
4.3.5 Buffers .....	33
4.4 Fraction of Dissociating Species at a Given pH: $\alpha$ -Values .....	35
本章小结 .....	37
PROBLEMS .....	38

## Chapter 05

## Chapter 05 Acid-base Titrations

5.1 Strong acid strong base .....	39
5.2 Detection of the end point: indicators .....	41
5.3 Acid versus base .....	43
5.3.1 Weak acid versus strong base .....	43
5.3.2 Titration of polyprotic acid .....	46
5.3.3 Mixtures of acid or base .....	46
5.4 Preparation of standard base solutions .....	48
5.5 Preparation of standard acid solutions .....	49
本章小结 .....	49
PROBLEMS .....	51

## Chapter 06

## Chapter 06 Complexometric Titrations

6.1	Complexes; formation constants	53
6.2	Chelates; EDTA	54
6.2.1	Metal-EDTA formation constants	55
6.2.2	EDTA is a weak acid	55
6.2.3	The formation constant	55
6.2.4	EDTA must compete with other ligands	56
6.3	EDTA titration curves	57
6.3.1	Calculating the titration curve	57
6.4	Detection of the end point; indicators	60
6.5	High purity EDTA	62
6.6	Fraction of dissociating species in polyligand complexes; $\beta$ -values	63
	本章小结	65
	PROBLEMS	66

## Chapter 07

## Chapter 07 Reduction-Oxidation Titrations

7.1	Principles	67
7.2	Electrochemical cells	68
7.3	The Nernst equation	70
7.4	Calculation of the equilibrium constant of a reaction	72
7.5	Titration curves	73
7.6	Detection of the end point	76
7.6.1	Self-indication	76
7.6.2	Starch indicator	77
7.6.3	Redox indicators	77
7.7	Formal potential	78
7.7.1	Dependence of potential on pH	79
7.7.2	Dependence of potential on complexation	79
7.8	Limitations of electrode potentials	80
7.9	Titrations involving Iodine: iodimetry and iodometry	80
7.9.1	Iodimetry	80
7.9.2	Iodometry	82
7.10	Titrations with oxidizing agents	83
7.11	Titration with reducing agents	86
7.12	Preparation of the analyte solution	86
	本章小结	88
	PROBLEMS	89

**Chapter 08****Chapter 08 Precipitation Titrations**

8.1	Effect of acidity on solubility of precipitates .....	91
8.2	Precipitation titrations .....	93
8.2.1	Titration curves .....	93
8.2.2	Detection of the end point; indicators .....	95
	本章小结 .....	98
	PROBLEMS .....	99

**Chapter 09****Chapter 09 Gravimetric Analysis**

9.1	Precipitation equilibria; the solubility product .....	101
9.2	The diverse ion effect on solubility; $K_{sp}$ .....	102
9.3	Unit operations in gravimetric analysis .....	103
9.3.1	Steps of gravimetric analysis .....	103
9.3.2	Conditions for analytical precipitation .....	104
9.3.3	Digestion of the precipitate .....	105
9.3.4	Impurities in precipitates .....	107
9.3.5	Washing and filtering the precipitates .....	108
9.3.6	Drying or igniting the precipitate .....	109
9.3.7	Homogeneous precipitation .....	110
9.4	Examples of gravimetric analysis .....	111
	本章小结 .....	111
	PROBLEMS .....	112

**Chapter 10****Chapter 10 Spectroscopic Methods of Analysis**

10.1	What is electromagnetic radiation .....	114
10.1.1	Wave properties of electromagnetic radiation .....	114
10.1.2	Particle properties of electromagnetic radiation .....	115
10.2	Spectroscopy based on absorption .....	116
10.2.1	Absorbance of electromagnetic radiation .....	116
10.2.2	UV/Vis spectra for molecules and ions .....	116
10.3	Transmittance and absorbance .....	118
10.4	Absorbance and concentration; Beer's law .....	119
10.5	Beer's law and multicomponent samples .....	120
10.6	Limitations to Beer's law .....	120
10.6.1	Fundamental limitations to Beer's law .....	120



10.6.2	Chemical limitations to Beer's law	121
10.6.3	Instrumental limitations to Beer's law	121
本章小结		122
PROBLEMS		123

## Chapter 11 Analytical Separation

11.1	Classifying separation techniques	125
11.1.1	Separation by precipitation	125
11.1.2	Extraction between two phases	127
11.1.3	Liquid-liquid extractions	127
11.2	Partition coefficients and distribution ratios	128
本章小结		130

## Chapter 12 Pollution Analysis

12.1	Air analysis	131
12.1.1	Air sample collection	131
12.1.2	Air sample analysis	134
12.2	Water analysis	134
12.2.1	Sampling of water	135
12.2.2	Analysis of water samples	135

Appendix		139
----------	--	-----

References		139
------------	--	-----

# Chapter 01

## Introduction

*Chemistry is the study of matter, including its composition, structure, physical properties, and reactivity. They are many approaches to studying chemistry, but, for convenience, we traditionally divide it into five fields: organic, inorganic, physical, biochemical, and analytical. Although this division is historical and arbitrary, as witnessed by the current interest in interdisciplinary areas such as bioanalytical and organometallic chemistry, these five fields remain the simplest division spanning the discipline of chemistry.*

*Training in each of these fields provides a unique perspective to the study of chemistry. Undergraduate chemistry courses and textbooks are more than a collection of facts; they are a kind of apprenticeship. In keeping with this spirit, this text introduces the field of analytical chemistry and the unique perspectives that analytical chemists bring to the study of chemistry.*

### 1.1 What is analytical chemistry

Analytical chemistry can be thought of as comprising two branches, qualitative and quantitative. Qualitative analysis deals with finding what constituents are in an analytical sample, and quantitative analysis deals with the determination of how much of a given substance is in the sample. In the latter case, a history of the sample composition will generally be known; or else the analyst will have performed a qualitative test. With today's instrumentation and with the large variety of chemical measurements available, specificity or sufficient. Selectivity can often be achieved so that the quantitative measurement serves as a qualitative measurement. However, simple qualitative tests are usually more rapid than quantitative procedures. Qualitative analysis is composed of two fields: inorganic and organic. The former is usually covered in introductory chemistry

Chapter

1

Chapter

2

Chapter

3

Chapter

4

Chapter

5

Chapter

6

Chapter

7

Chapter

8

Chapter

9

Chapter

10

Chapter

11

Chapter

12

Appendix

courses, whereas the latter is best left until after the student has had a course in organic chemistry. This text deals principally with quantitative analysis. In the consideration of applications of different techniques, examples are drawn from the life sciences, clinical chemistry, air and water pollution analysis, occupational health and safety applications, and industrial analysis.

## 1.2 Measurement of the analyte

The method employed for the actual quantitative measurement of the analyte will depend on a number of factors, not the least important being the amount of analyte present and the accuracy required. Many available techniques possess varying degrees of selectivity, sensitivity, accuracy and precision, and rapidity. Gravimetric analysis usually involves the selective separation of the analyte by precipitation, followed by the very nonselective measurement of mass (of the precipitate). In volumetric or titrimetric analysis, the analyte reacts with a measured volume of reagent of known concentration, in a process called titration. A change in some physical or chemical property of the sample, for example, an electrical property or the absorption of electromagnetic radiation.

## 1.3 Range

Analytical methods are often classed according to size of sample. Such classification is arbitrary and there is no sharp dividing line. The analysis may be classed as macro, semimicro, micro, or ultramicro. Table 1.1 gives approximate classifications according to sample mass or volume. The volume classifications are those employed in clinical laboratories. Special handling technique and balances for weighing are required for micro and ultramicro operations.

Table 1.1 Classification of Analytical methods to Size of Sample

Method	Sample mass/mg	Sample Volume/ $\mu$ l
Macro	>100	>100
Semimicro	10~100	50~100
Micro	1~10	<50
Ultramicro	<1	

The constituents on the sample may be classified as major ( $>1\%$ ), minor ( $0.1\% \sim 1\%$ ), or trace ( $<0.1\%$ ). A few parts per million of a constituent might be classed as ultratrace.

An analysis may be complete or partial; that is, either all constituents or only selected constituents may be analyzed. Most often, the analyst is requested to report on a

specified chemical or chemicals.

## 1.4 The analytical perspective

Having noted that each field of chemistry brings a unique perspective to the study of chemistry, we now ask a second deceptively simple question. What is the “analytical perspective”? Many analytical chemists describe this perspective as an analytical approach to solving problems. Although there are probably as many descriptions of the analytical approach as there are analytical chemists, it is convenient for our purposes to treat it as a five-step process:

- (1) Identify and define the problem.
- (2) Design the experimental procedure.
- (3) Conduct an experiment, and gather data.
- (4) Analyze the experimental data.
- (5) Propose a solution to the problem.

Analytical chemistry begins with a problem, examples of which include evaluating the amount of dust and soil ingested by children as an indicator of environmental exposure to particulate based pollutants, resolving contradictory evidence regarding the toxicity of perfluoro polymers during combustion, or developing rapid and sensitive detectors for chemical warfare agents. At this point the analytical approach involves a collaboration between the analytical chemist and the individuals responsible for the problem. Together they decide what information is needed. It is also necessary for the analytical chemist to understand how the problem relates to broader research goals. The type of information needed and the problem’s context are essential to designing an appropriate experimental procedure.

Designing an experimental procedure involves selecting an appropriate method of analysis based on established criteria, such as accuracy, precision, sensitivity, and detection limit; the urgency with which results are needed; the cost of a single analysis; the number of samples to be analyzed; and the amount of sample available for analysis. Finding an appropriate balance between these parameters is frequently complicated by their interdependence. For example, improving the precision of an analysis may require a larger sample. Consideration is also given to collecting, storing, and preparing samples, and to whether chemical or physical interferences will affect the analysis. Finally, a good experimental procedure may still yield useless information if there is no method for validating the results.

The most visible part of the analytical approach occurs in the laboratory. As part of the validation process, appropriate chemical or physical standards are used to calibrate

Chapter

1

Chapter

2

Chapter

3

Chapter

4

Chapter

5

Chapter

6

Chapter

7

Chapter

8

Chapter

9

Chapter

10

Chapter

11

Chapter

12

Appendix



any equipment being used and any solutions whose concentrations must be known. The selected samples are then analyzed and the raw data recorded.

The raw data collected during the experiment are then analyzed. Frequently the data must be reduced or transformed to a more readily analyzable form. A statistical treatment of the data is used to evaluate the accuracy and precision of the analysis and to validate the procedure. These results are compared with the criteria established during the design of the experiment, and then the design is reconsidered, additional experimental trials are run, or a solution to the problem is proposed. When a solution is proposed, the results are subject to an external evaluation that may result in a new problem and the beginning of a new analytical cycle.

Analytical chemistry begins with a problem, examples of which include evaluating the amount of dust and soil ingested by children as an indicator of environmental exposure to particulate based pollutants, resolving contradictory evidence regarding the toxicity of perfluoro polymers during combustion, or developing rapid and sensitive detectors for chemical warfare agents. At this point the analytical approach involves a collaboration between the analytical chemist and the individuals responsible for the problem. Together they decide what information is needed. It is also necessary for the analytical chemist to understand how the problem relates to broader research goals. The type of information needed and the problem's context are essential to designing an appropriate experimental procedure.

Designing an experimental procedure involves selecting an appropriate method of analysis based on established criteria, such as accuracy, precision, sensitivity, and detection limits. The urgency with which results are needed, the cost of a single analysis, the number of samples to be analyzed, and the amount of sample available for analysis. Finding an appropriate balance between these parameters is frequently complicated by their interdependence. For example, improving the precision of an analysis may require a larger sample. Consideration is also given to collecting, storing, and preparing samples, and to whether chemical or physical interferences will affect the analysis. Finally, a good experimental procedure may still yield useless information if there is no method for validating the results.

The most visible part of the analytical approach occurs in the laboratory. As part of the validation process, appropriate chemical or physical standards are used to calibrate

- (1) Identify and define the problem.
- (2) Design the experimental procedure.
- (3) Conduct an experiment, and gather data.
- (4) Analyze the experimental data.
- (5) Propose a solution to the problem.

## Chapter 02

# Errors and Data Treatment in Quantitative Analysis

*Although data handling normally follows the collection of data in an analysis, it is treated early in the text because a knowledge of statistical analysis will be required as you perform of the data that are collected and therefore to set limitations on each step of the analysis. The design of experiments (including size of sample required, accuracy of measurements required, number of analyses needed, and so forth) is determined from a proper understanding of what the data will represent.*

## 2.1 Determinate errors

Two main classes of errors can affect the accuracy or precision of a measured quantity. Determinate errors are those that, as the name implies, are determinable and that presumably can be either avoided or corrected. They may be constant, as in the case of an uncalibrated weight that is used in all weighings. Or, they may be variable but of such a nature that they can be accounted for and corrected, such as a buret whose volume readings are in error by different amounts at different volumes.

The error can be proportional to sample size, or may change in a more complex manner. More often than not, the variation is unidirectional, as in the case of solubility loss of a precipitate (negative error). It can, however, be random in sign. Such an example is the change in solution volume and concentration occurring with changes in temperature. Such measurable determinate errors are classed as systematic errors.

Some common determinate errors are:

(1) Instrumental errors These include faulty equipment, uncalibrated weights, and uncalibrated glassware.

Chapter

1

Chapter

2

Chapter

3

Chapter

4

Chapter

5

Chapter

6

Chapter

7

Chapter

8

Chapter

9

Chapter

10

Chapter

11

Chapter

12

Appendix

(2) Operative errors These include personal errors and can be reduced by experience and care of the analyst in the physical manipulations involved. Operations in which these errors may occur include transfer of solutions, effervescence and “bumping” during sample dissolution, incomplete drying of samples, etc. These are difficult to correct for. Other personal errors include mathematical errors in calculations and prejudice in estimating measurements.

(3) Errors of the method These are the most serious errors of an analyst. Most of the above errors can be minimized or corrected for, but errors that are inherent in the method cannot be changed unless the conditions of the determination are altered. Some sources of methodic errors include coprecipitation of impurities, slight solubility of a precipitate, side reactions, incomplete reactions, impurities in reagents, and so forth, sometimes correction can be relatively simple, for example by running a reagent blank. A blank determination is an analysis on the added reagents only. It is standard practice to run such blanks and to subtract the results from those for the sample. When errors become intolerable, another approach to the analysis must be made. Sometimes, however, we are forced to accept a given method in the absence of a better one.

## 2.2 Indeterminate errors

The second class of errors includes the indeterminate errors, often called accidental or random errors. They are revealed by small differences in successive measurements made by the same analyst under virtually identical conditions, and they cannot be predicted or estimated. These accidental errors will follow a random distribution; therefore, mathematical laws of probability can be applied to arrive at some conclusion regarding the most probable result of a series of measurements.

Indeterminate errors really originate in the limited ability of the analyst to control or make corrections for external conditions, or in his inability to recognize the appearance of factors that will result in errors. Some random errors stem from the more statistical nature of things, for example, nuclear counting errors. Sometimes, by changing conditions, some unknown error will disappear. Of course, it will be impossible, to eliminate all possible random errors in an experiment and the analyst must be content to minimize them to a tolerable or insignificant level.

## 2.3 Accuracy and precision

**Accuracy** is the degree of agreement between the measured value and the true value. An absolute true value is seldom known. A more realistic definition of accuracy,

then, would assume it to be the agreement between a measured value and the accepted true value.

Wu can by good analytical technique, such as making comparisons against a known standard sample of similar composition, arrive at a reasonable assumption about the accuracy of a method, within the limitations of the knowledge of the “known” sample (and of the measurements). The accuracy to which we know the value of the standard sample is ultimately dependent on some measurement that will have a given limit of certainty in it. **Precision** is defined as the degree of agreement between replicate measurements of the same quantity. That is, is the repeatability of a result. Good precision does not assure good accuracy. This would be the case, for example, if there were a systematic error in the analysis. A weight used to measure each of the samples may be in error. This error does not affect the precision, but it does affect the accuracy. On the other hand, the precision can be relatively poor and the accuracy, more or less by chance, might be good. Since all real analyses are unknown, the higher the degree of precision, the greater the chance of obtaining the true value. It would be fruitless to hope that a value is accurate if the precision is poor, and the analytical chemist strives for repeatable results to assure the highest possible accuracy.

As we shall see later, the more measurements that are made, the more reliable will be the measure of precision. The number of measurements required will depend on the accuracy required and on the known reproducibility of the method.

### 2.3.1 Ways of expressing accuracy

There are various ways and units in which the accuracy of a measurement can be expressed, an accepted true value for comparison being assumed.

(1) **Absolute Error** The difference between the true value and the measured value, with regard to the sign, is the absolute error, and it is reported in the same units as the measurement. If a 2.62 g sample of material is analyzed to be 2.52 g, the absolute error is  $-0.10$  g. If the measured value is the average of several measurements, the error is called the mean error. The mean error can also be calculated by taking the average difference, with regard to sign, of the individual test results from the true value.

$$E = x - T \quad (2.1)$$

(2) **Relative Error** The absolute or mean error expressed as a percentage of the true value is the relative error. The above analysis has a relative error of  $(-0.10/2.62) \times 100\% = -3.8\%$ . The relative accuracy is the measured value or mean expressed as a percentage of the true value. The above analysis has a relative accuracy of  $(2.52/2.62) \times 100\% = 92.6\%$ . We should emphasize that neither is known to be “true” and the relative error

Chapter

1

Chapter

2

Chapter

3

Chapter

4

Chapter

5

Chapter

6

Chapter

7

Chapter

8

Chapter

9

Chapter

10

Chapter

11

Chapter

12

Appendix



or accuracy is based on the mean of two sets of measurements.

$$E_r = \frac{E}{T} \times 100\% \quad (2.2)$$

The relative error can be expressed in units other than percentages. In very accurate work, we are usually dealing with relative errors of less than 1%, and it is convenient to use a smaller unit. A 1% error is equivalent to 1 part in 100. It is also equivalent to 10 parts in 1000. This latter unit is commonly used for expressing small uncertainties. That is, the uncertainty is expressed in parts per thousand, written as ppt. The number 23 expressed as parts per thousand of the number 6725 would be 23 parts per 6725 or 3.4 ppt. Parts per thousand is often used in expressing precision of measurement.

### 2.3.2 Ways of expressing precision

Each set of analytical results should be accompanied by an indication of the precision of the analysis. Various ways of indicating precision are acceptable.

(1) Average Deviation The average deviation of the measurements of a set is the mean of the differences of the individual measurements and the mean of the measurements, without regard to sign.

$$\bar{d} = \frac{\sum_{i=1}^n |x_i - \bar{x}|}{n} \quad (2.3)$$

$$\bar{d} = \frac{|d_1| + |d_2| + \dots + |d_n|}{n} = \frac{1}{n} \sum_{i=1}^n |d_i| \quad (2.4)$$

(2) Standard Deviation The standard deviation,  $\sigma$ , of an infinite set of experimental data is theoretically the square root of the mean of the squares of the difference between the individual measured values,  $x_i$ , and the mean of the infinite number of measurements,  $\mu$  (which should represent the “true” value).

$$\sigma = \sqrt{\frac{\sum (x_i - \mu)^2}{n}} \quad (2.5)$$

This equation holds strictly only as  $n \rightarrow \infty$ . In practice, we must calculate the individual deviations from the mean of a limited number of measurements,  $\bar{x}$ , in which it is anticipated that  $\bar{x} \rightarrow \mu$ , although we have no assurance this will be so.

For a set of  $n$  measurements, it is possible to calculate  $n$  independently variable deviations from some reference number. But if the reference number chosen is the estimated mean,  $\bar{x}$ , the sum of the individual deviations (retaining signs) must necessarily add up to zero, and so values of  $n-1$  deviations are adequate to define the  $n$ th. That is, there are only  $n-1$  independent deviations from the mean; when  $n-1$  values have been selected, the last is predetermined. We have, in effect, used one degree of freedom of the data in calculating the mean, leaving  $n-1$  degrees of freedom for calculating the precision.