A Manual for the CHEMICAL ANALYSIS of METALS

THOMAS R. DULSKI

ASTM

A Manual for the Chemical Analysis of Metals

Thomas R. Dulski

ASTM Manual Series: MNL 25
ASTM Publication Code Number (PCN)
28-025096-50

100 Barr Harbor Drive, West Conshohocken, PA 19428-2959

Library of Congress Cataloging-in-Publication Data

Dulski, Thomas R., 1942–
A manual for the chemical analysis of metals/Thomas R. Dulski.
p. cm.—(ASTM manual series; MNL 25)
Includes bibliographical references (p. –) and Index.
ISBN 0-8031-2066-4
1. Metals—Analysis—Handbooks, manuals, etc. I. Title.
II. Series.
QD132.D85 1996
669'.92–dc20 96-1836
CIP

NOTE: This manual does not purport to address (all of) the safety problems associated with its use. It is the responsibility of the user of this manual to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

Printed in Ann Arbor, MI
March 1996

Dedication

THIS BOOK IS DEDICATED to my father, Frank Dulski, who was both a gentleman and a gentle man.

Acknowledgments

THERE ARE three levels of indebtedness that I would like to acknowledge. First, there are those individuals, living and deceased, who for over 32 years have taught me from their deep knowledge of classical and instrumental analysis: Charles J. Byrnes, Silve Kallmann, Ralph M. Raybeck, James O. Strauss, Alfons Suk, and George Vassilaros. These cherished friends have contributed to this book in countless unrecognized ways. Next, there are those who have given their time and their efforts in the review of the manuscript: their names and affiliations are listed below. The suggestions and corrections of these individuals have been an invaluable aid in the preparation of the final text. Finally, there are my friends, coworkers, and associates, including the members of ASTM Committee E-1, and my family—my wife, Grace, my daughter, Brittany, and my mother, Stephanie—who have in their respective ways supported and sustained me in this work. Thank you, all.

Terry F. Beckwith
Zinc Corporation of America
Monaca, PA

Charles J. Byrnes
Crucible Materials Corp.—
Research Center
Pittsburgh, PA

Robert N. Smith, retired
American Cast Iron Pipe Co.
Birmingham, AL

Jeffrey C. Morrow
Colonial Metals Co.—Lab
Columbia, PA

Charles M. Beck
NIST
Gaithersburg, MD

D. A. Flinchbaugh
Bethlehem Steel Corp.
Bethlehem, PA

Charles K. Deak
C. K. Deak Technical Services, Inc.
Warren, MI

Foreword

THIS PUBLICATION, *A Manual for the Chemical Analysis of Metals,* was approved by ASTM Committee E-1 on Analytical Chemistry for Metals, Ores, and Related Materials. This is Manual 25 in ASTM's manual series.

Cover photo from the collection of Isabel and Alfred Bader.

Disclaimer

MUCH OF THE METHODOLOGY described in this book is potentially hazardous. The author, his affiliation, Carpenter Technology Corporation, and the publisher, ASTM, assume no liability whatsoever for any material, financial, or personal loss or injury incurred from the implementation of the equipment, chemicals, or procedures described herein.

Contents

Introduction

WHILE THE ANCIENTS WERE intuitively aware of the particulate nature of matter and had developed a keen understanding of proportions and mathematics, it was not until the eighteenth century, when the mists of alchemy began to clear, that mankind first peeked into the heart of a substance. The insights that followed were in every sense as profound as those that followed the somewhat earlier ponderings of force and light. Analytical chemistry, as a more or less clearly defined discipline, has been around now for about 200 years. The intimate connection between the analysis of materials and the understanding of the laws governing their nature has remained a hallmark and an impetus of both since that time.

Among the earliest insights of those nascent days was the very notion that certain substances were, in fact, divisible. Air, for example. Leonardo da Vinci had suspected and Joseph Priestley had proved that it was a mixture, but Antoine Lavoisier gave *quantity* to its components. And today, watching those two perfectly proportioned peaks emerge when a sample of air is injected into a gas chromatograph, who can deny a key historical role to compositional analysis?

The analysis of metals was among the earliest applications of analytical chemistry, but it is also interesting to note that fire assay techniques used to assess the purity of gold antedated the scientific discipline by 3000 years. In the nineteenth century, the Bessimer process (introduced in 1856) made the large-volume production of steel a reality. This was followed shortly by the open-hearth (1864) and electric furnace (1890) processes. The latter led to the production of high-purity alloy steels and the need for accurate quantitative measurement of product composition. Brass and bronze foundries, derived from a centuries-old tradition, began to employ new processes and to produce new alloys. And in the 1890s the Hall process gave birth to the aluminum industry. Each of these developments required innovations from analytical chemistry—to analyze their products and raw materials, to assess their recoveries, and to fine tune their processes.

In the second half of the twentieth century, nickel- and cobalt-base high-temperature alloys came into their own for critical aerospace applications, followed closely by titanium alloys. The nuclear industry required zirconium and beryllium alloys. These and other metals industries made unprecedented demands on the analytical chemist for accuracy, precision, and sensitivity. And at the same time, the new high-speed production processes in "traditional" industries—the basic oxygen furnace, the argon-oxygen decarburization (AOD) vessel, the continuous caster—were adding a new demand for nearly instantaneous results.

The evolution of techniques for the analysis of metals and alloys followed these metallurgical developments very closely.[1] Late nineteenth and early twentieth century metals analysis laboratories employed gravimetric and titrimetric methods. As the demand for timely reports increased, time-honored approaches were modified. Factor weights and burets calibrated in element percent circumvented time-consuming hand calculations. A major innovation at the time was the color intensity comparator, a subjective application of Beer's law. In the 1920s and 1930s instrumentation began to ease the analyst's burden: pH meters, filter photometers, electrogravimetric analyzers.

But it was in the 1940s that instrumental approaches began to dominate. Spectrophotometers extended molecular absorption approaches to new levels of sensitivity and

[1]For a brief chronology of the developments in both fields, see Appendix I.

broadened the useful wavelength range to the near ultraviolet and infrared. Emission spectroscopy became a practical tool. In the 1950s, X-ray fluorescence began to revolutionize the field, taking the idea of rapid analysis into a new realm. In the 1960s, atomic absorption spectrophotometry promised a revolution in solution-based analysis. In the 1970s and 1980s, it was the plasma emission techniques. Today, inorganic mass spectrometry appears poised to take the lead, and computerization promises a paperless lab. Each of those past developments has delivered nearly all that it had initially promised, and each has contributed immeasurably to the metals industry.

Today, a modern control laboratory in, for example, a large integrated steel mill can deliver analytical results for 25 elements to two or three decimal-place accuracy within 5 min of receipt of the sample. And work is now underway to develop robot labs and furnace-side probes for even faster compositional analysis. The size of the work force in a large steel mill laboratory has dropped from several hundred before World War II to, perhaps, 15 to 20 today. And the new robot laboratories have further reduced the personnel required to two or three largely maintenance positions. Such robot facilities incorporate completely automated sample preparation and may include optical emission and X-ray fluorescence spectrometers and carbon, sulfur, oxygen, and nitrogen determinators. The instruments automatically select and run standards, and if validation criteria are not met, they automatically recalibrate themselves.

One would think by pondering this picture that the present and future needs of the metals industry are now well on their way to being adequately met. In fact, there are some dark clouds on this high-tech horizon. To properly describe the problem, it is necessary to first point out some fundamental distinctions in the formalism by which a substance can be analyzed. In the days when gravimetry and titrimetry were the only options available for a metals analyst, results were being generated independent of any matrix-matched certified reference material. These are sometimes termed *definitive* methods, and even today there are only a few techniques that can be added to the list (coulometry and isotope dilution mass spectrometry come immediately to mind). In gravimetry, a pure compound (or element) is weighed and related to the analyte's abundance in the test material. In volumetric work based on normality, the analyte reacts with a precisely measured amount of a pure compound. In both cases, the only function for a certified metal alloy standard is to *validate* the skill of the operator.

The situation changed in a fundamental way when high-speed instrumental methods began to be introduced. Optical emission and X-ray fluorescence spectrometers for all their blinding speed are powerless to operate without metal alloy standards. So much so, in fact, that an argot of terms has formed around the subject. Thus we have "drift standards," "type standards," "calibration standards," "standardization standards," "control standards," "precontrol standards," and several others. Similarly, modern carbon, sulfur, nitrogen, oxygen, and hydrogen determinators are designed with metal alloy standards as their primary means of calibration. These methods are said to be *comparative*. We have traded for speed, and what we gave up was independence.

And so today there are uncounted numbers of standards in metals analysis laboratories throughout the world. Each lab has its small or large personalized suite, selected to meet its particular requirements. Many of these have been purchased over many years from standardizing agencies like the National Institute of Standards and Technology (formerly, the National Bureau of Standards). Some are cherished remnants of days when classical chemical analysis was being used to develop "in-house" standards for instrument calibration. For the sad truth is that few organizations have had the foresight to retain *any* wet chemical analysis capability, let alone the ability to perform definitive methods. Moreover, while the resources available to standardizing agencies, governmental or private, have always been limited, the traditionally employed interlaboratory cooperative round robin is breaking down because the ability to perform the necessary work no longer exists.

Each time a solid spectrometric standard is resurfaced, some material is lost and stocks of standards available for sale are being exhausted. Often they are replaced with reference materials whose certificate values show much greater uncertainty. Even more often, they are not being replaced at all.

The result of this trend will be a deterioration in the veracity of the results produced by those high-speed/low-overhead analytical engines. For undoubtedly some will suggest that we make a standard by *comparing* it to a standard, ignoring the enormous potential for runaway systematic error, and, like a photograph copied from a copy, truth

will quickly blur. The alternatives will be almost equally painful to sharp-penciled accountants—either allow those speedy engines to grind to a halt or reinstate some sort of "wet lab" to work on standards.

The situation is, perhaps, not quite as bleak as I have just pictured. In certain metals companies (not always the largest), and particularly in metals research facilities, some classical analytical chemistry is still in evidence. Besides the need for in-house standards, there are a number of excellent practical reasons for maintaining a "wet lab." First, the great flexibility of chemical techniques can accommodate many sample sizes and shapes (fine wire or small parts, for example) that are difficult or impossible by solids spectrometric methods. Unlike those approaches, chemical methods can effectively handle a moderate degree of sample inhomogeneity by linking wet chemistry to a rational sampling plan. Chemical methods are immune to thermal history effects that sometimes harass solids techniques. Chemical techniques *may* be more accurate, more precise, or more sensitive than particular solids spectroscopic approaches. Certainly they are *different* and thus represent a valuable check on data quality and can serve as umpires between instruments, between laboratories, and between vendor and consumer industries. In the absence of suitable standards, sometimes a classical definitive method is contractually specified as part of a compositional certification test plan for a key element in a critical application alloy.

Such agreements are rare, however. The fact is the definitive methods, in the strict application of that term, are rare as well. Today, much of what remains of wet analytical chemistry occupies a mid-ground between definitive and comparative protocols. Currently, what many call "wet analysis" consists of dissolving the sample, diluting it to some fixed volume, and presenting it to some instrument that has been calibrated with pure (or matrix-matched) solutions of the analyte.

While this methodology evinces all the advantages associated with a solution-based approach, it is fraught with potential errors: calibrant purity, linearity limits, spectroscopic line interferences, and chemical effects, to name a few. It is reasonably rapid, however, and requires only a moderate degree of manipulative skill. Spectroscopic knowledge is needed, of course, to anticipate line overlaps and sensitivity problems, but the solutions found for these problems are typically instrumental ones: alternate line selection, interelement correction factors, off-peak background correction, and others. It rarely occurs to today's analysts that many classical chemical separation schemes are directly applicable to spectroscopic problems. And yet just such a hybrid classical/instrumental approach often yields the highest quality analysis in the least amount of time. As a cost-effective measure when the best level of work is needed and solids techniques are not a viable option, returning to the chemistry in this way makes sense.

Which leads us finally to the *raison d'etre* of this book. The last quarter of the twentieth century has witnessed a prodigious loss of classical analytical chemistry lore from the industrial workplace. I have used the word "lore" advisedly, because other aspects of this discipline—theory, good laboratory practices, and specific methods—can still be extracted from public, university, and industrial libraries. But with the exception of a few long-out-of-print and somewhat dated texts, there is no source from which to learn the thinking and manipulative skills that make a classical analyst. "Lore" also implies a degree of art that must accompany the science—the things that work even though their chemistry is poorly understood.[2] But the unfortunate fact is that most of the lore has been lost as wet labs were closed and classical analysts were retired without replacement. As we have seen, these decisions have been short-sighted and potentially disastrous.

An equally disturbing trend is the recent spread into industry laboratories of a dogma, widely held by lawyers and bureaucrats, that any human act, no matter how involved and complex, can be precisely specified in a written set of instructions. This credo is patently false, as anyone who reflects a moment on the works of man can plainly see. That is why there is only one Sistine Chapel ceiling, why all violins do not sound like a Stradivarius, and why open heart surgery is not offered as a correspondence school course. The simple fact is that no written protocol, even when the last "t" is crossed and the last "i" is dotted, can ever reduce the analyst to that hypothetical "pair of hands"—

[2]The notion of lore is not new to science, nor is it antiscience. Rather, it precedes science. How many lives have been saved, for example, by drugs whose mode of action is only dimly understood?

a cheap, readily available, ultimately disposable "human resource," in the ultimate implication of that term. Well-written analytical procedures, such as ASTM standard methods are, of course, indispensable recipes, but one does not become a great chef, or even a good cook, by reading recipes.

This book is an attempt to describe and explain some of the intangibles and many of the details associated with the analysis of metals. It is not a recipe book of specific methods, but rather a training manual and a reference source that can complement a laboratory quality control manual and a suitable array of analytical procedures. Emphasis has been placed on skills, knowledge, and approaches to problem solving that are typically not described in either QC manuals or specific method documents. Clearly, no book can summarize all the tricks of this or any other trade with sufficient detail to substitute for a good "hands-on" on-the-job training program. But modern industrial realities being what they are, the time and talent for such programs is no longer available. The knowledge in many cases has been lost. Lone analysts are frequently placed in the position of either sinking or swimming along a *tsunami* of a learning curve. And because few have the time or resources for an adequate literature search, the wheel is reinvented many times.

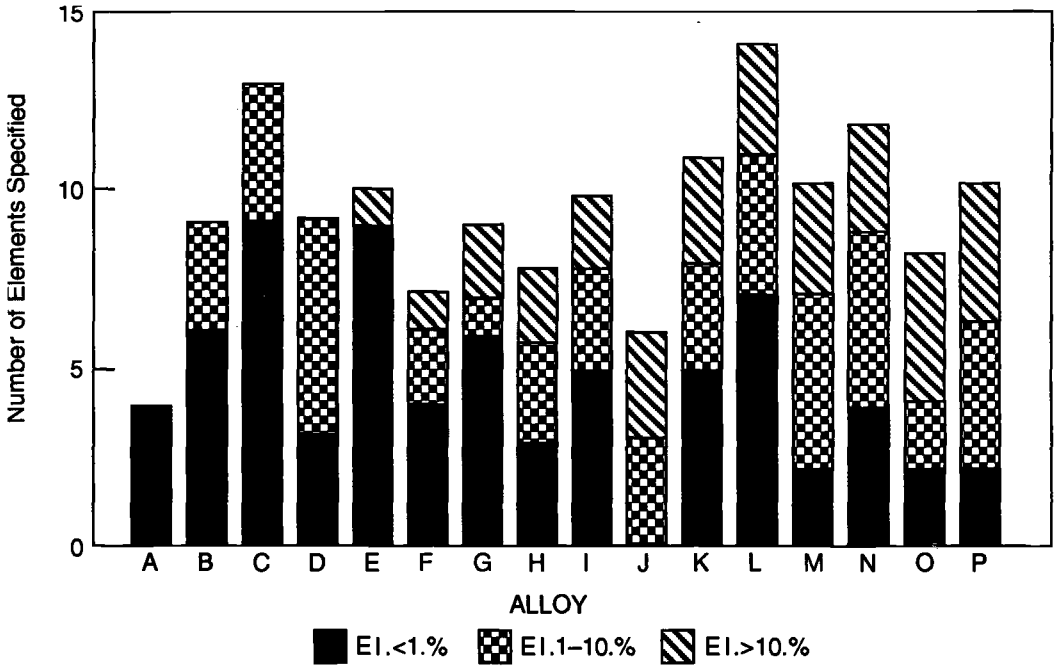
And so, what is being attempted here is to provide some guidance for those who find themselves alone in the trenches, perhaps professionally trained in chemistry, but inexperienced in the trade of metals analysis. They may be alone or in charge of a staff of inexperienced or partially trained personnel. They may have access to high-speed spectrometers and other equipment that has been purchased to lower overhead costs, but that never quite meets all the demands placed upon it.

Unfortunately, academic credentials are an inadequate preparation for this sort of career. The universities and colleges have de-emphasized analytical chemistry and, in particular, classical analytical chemistry. And descriptive inorganic chemistry has largely been replaced by theory. While these changes may serve larger needs, they have hurt certain pragmatic concerns, among them, metals analysis. It is entirely possible that an individual may be awarded a Ph.D. in chemistry and have no idea of the colors of vanadium ion in aqueous solution. This observation is not meant to reflect on individual achievement, academic standards, or the quality of academic programs, but simply to illustrate that industry's perhaps parochial concerns are not being met. Certainly college training provides the foundation for scientific problem solving, and any specific fact can be extricated, but no one has bothered to inform the industrial marketplace that all their problems may not be instantly solved by their next hire.

Training in another related field of industrial analytical chemistry can be a useful preparation for an assignment in metals analysis; however, the professional manager type of individuals may find themselves adrift without the technical knowledge to guide their staff. Today, with the analytical workforce severely limited in size and often shrinking, technical guidance from management is required much more urgently than in earlier times when expertise could emanate from a line of "sublieutenants."

The complexity of the analytical task, of course, varies widely between industry laboratories. Some are called upon to analyze comparatively few metal alloy compositions, while 500 standard stocks are not uncommon in others. A research environment or a "jobber" type of mill is much more likely to routinely encounter the nonroutine. One measure of the comparative complexity of the work is the number and frequency of measured analytes and, in particular, the number and frequency of such analytes present at levels of 10% and above (since the need for wet chemical support increases dramatically at about that level). This point is illustrated in Fig. I-1, which uses a few selected alloys from a number of metals industries to suggest trends. A metals analyst may in the course of a career analyze half a hundred different elements in major, minor, and trace amounts. High-temperature superalloys, in particular, represent a challenge to the analyst; their only rival in the inorganic field may be in the complex area of mineral analysis.

It should also be recognized that few laboratories are exclusively engaged in metals analysis. Most are also called upon to analyze an array of other materials—slags, refractories, water, air particulates, process gases, plating and pickling baths, and a host of other materials. While these are not the main subject of this volume, they are part of the overall task and thus cannot be completely ignored. Many of the skills, some of the separations, and a lot of the thinking involved in solving metals analysis problems are directly transferrable to other matrices.



NOTE: See key below for alloy designations.

A: Plain Carbon Steel (AISI 1040)
B: Alpha-Beta Titanium Alloy (UNS R56620)
C: High-Strength Low Alloy Steel (ASTM A871)
D: High-Speed Tool Steel (AISI M42)
E: Wrought Aluminum (AA No. 1070)
F: Ferritic Stainless Steel (AISI 405)
G: Cast Aluminum Alloy (AA No. 384.2)
H: Austenitic Stainless Steel (AISI 316L)
I: Aluminum Bronze (Copper No. C63020)
J: Permanent Magnet Alloy (Alnico 9)
K: Iron-base High Temperature Alloy (A286; ASTM A-453)
L: Nickle-base High Temperature Alloy (Waspaloy; AISI 685)
M: Cobalt-base High Temperature Alloy (S-816; AMS 5765)
N: Nickle-base High Temperature Alloy (AF115)
O: Cobalt-base High Temperature Alloy (L605; AMS 5759)
P: Iron-base High Temperature Alloy (S-590; AMS 5770)

FIG. I-1—Frequency of analyte concentrations (miscellaneous alloy specifications).

The basic message of this book is: *Learn the chemistry*; know, at least in a general way, what is happening or expected to happen at each step in the analytical process. That *dictum* includes not just the ideal "paper" reactions of textbooks, but also the often ignored real-world deviations from ideal behavior—the way equilibria are shifted at high dilutions or the way cations are adsorbed on vessel walls, for example. That knowledge combined with an appropriate array of manipulative skills is principally the key to all forms of analytical problem solving. It is hoped that this book will be used as an aid in such problem solving for the analysis of metals. It is written for the laboratory technician, the chemist, and the lab manager who are faced with detection limit difficulties, or spectroscopic line interferences, with precision problems at high concentrations, or perhaps with an alloy that takes too long to dissolve.

Much of the material in this volume is gleaned from older ways of doing things, some is from the current literature, and some may never have been published before. Many of the older techniques and procedures are, of course, outdated and have been left to moulder on library shelves. But a judicious selection from the antiquarian lore still includes the most accurate and definitive procedures in many cases. And some of these methods contain manipulative steps that are valuable additions to the instrumental world of the sleek and the swift. I have tried my best to keep the focus on only those techniques that *can* and *should* be used today and in the years to come. Many of them will be needed only rarely, others will find use every day. But none have been included as curiosities. This is not a history.

The organization generally follows the analytical process: materials, samples, separations, measurement, and quality issues. There is also a large appendix that summarizes the analytically important chemical behavior of certain elements. Hopefully, this manual will be useful as a direct guide to specific problem solving.

Before closing this introduction, I must admit to at least two biases that may color the tone of this work. First, much of my own training and experience comes from the steel industry, in particular from that branch of the steel industry that produces specialty alloys. Second, I am by training and predilection a classical wet chemist. The former admission means that this book will have some leaning towards the problems related to iron-, nickel-, and cobalt-based alloys. The latter admission means that there will be a tendency to solve problems chemically, rather than by instrumental means. I do not believe that either bias will be fatal to my intended purpose since any addition to an analyst's bag of tricks has to be of some use. I am reminded of the introduction to that classic text, *Applied Inorganic Analysis*, where the authors compare the determination of an element in pure form to finger exercises, while its analysis in complex mixtures requires the skills of a virtuoso pianist. I think that in today's world of high-speed instruments and understaffed laboratories, the appropriate analogy is not Chopin but jazz. We must know when it is our turn to play, and we must know how to improvise.

REFERENCES

Beck, C. M., *Analytical Chemistry*, Vol. 66, No. 4, 1994, pp. 224A–239A.

Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley and Sons, New York, 1953.

Jaffe, B., *Crucibles: The Story of Chemistry*, Fawcett, Greenwich, CT, 1957.

Kallmann, S., *Analytical Chemistry*, Vol. 56, No. 9, 1984, pp. 1020A–1028A.

Slavin, W. and Epstein, M. S., Eds., *Spectrochimica Acta B* (Special Issue: *Reference Materials and Reference Methods*), Vol. 46B, No. 12, 1991, pp. 1571–1652.

Van Nostrand's Scientific Encyclopedia, 4th ed., Van Nostrand, Princeton, NJ, 1968.

Woldman's Engineering Alloys, 7th ed. , J. P. Frick, Ed., American Society for Metals International, Materials Park, OH, 1990, pp. 1425-1495.

About the Author

THOMAS R. DULSKI is an analytical chemist with 32 years of experience in the basic steel and specialty alloy industries. A graduate of the University of Pittsburgh, he has been employed by Crucible Materials Corporation, LTV Corporation, and for the last 22 years by Carpenter Technology Corporation.

Dulski is the author of 15 technical publications, including the book chapter "Classical Wet Analytical Chemistry" in the Materials Characterization volume of ASM's Metals Handbook series. He is a recipient of the Certificate of Appreciation, the Lundell–Bright and B. F. Scribner awards, and the title of Fellow from ASTM. In 1982 he received the Pharmacia Prize for the best paper published in *Talanta* by an industrial analytical chemist.

He served for many years as chairman of the ASTM Coordinating Committee on Standard Reference Materials for Metals, Metal Bearing Ores, and Related Materials. He is currently chairman of ASTM Committee E-1 on Analytical Chemistry for Metals, Ores, and Related Materials.

Dulski is the author of "Steel and Related Materials," which appears biennially in the Applied Reviews issue of the journal *Analytical Chemistry*.

ISBN 0-8031-2066-4