

ELECTRO- CHEMICAL ANALYSIS

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Electro-chemical analysis by Edgar F. Smith

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EDGAR F. SMITH

**ELECTRO-
CHEMICAL
ANALYSIS**

W. B. Rising

ELECTRO-CHEMICAL
ANALYSIS.

BY

EDGAR F. SMITH,

PROFESSOR OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA.

THIRD EDITION, REVISED AND ENLARGED.

With Thirty-nine Illustrations.

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1902.

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TO THE
ANNUAL

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PREFACE.

The first edition of this book appeared twelve years ago (1890). It was published then because the writer, after many years of experimentation, was convinced that the electric current had proved its right to be classed as a reagent in the quantitative determination and separation of metals. To-day the number of text-books relating to electro-chemical analysis, to the preparation of inorganic and organic compounds in the electrolytic way, and to the various theories of electrolysis has become quite large. There is scarcely a laboratory, where chemical analysis is taught, or where it is applied, in which use is not made of the "subtile agent" of Faraday.

Since the appearance (1894) of the second edition, as well as its German (1895) and French (1900) translations, numerous additions have been made to the domain of which the book especially treats; so that it was concluded to thoroughly revise the entire text. In doing this the author has abstained from any attempt to present the prevalent theories on electrolysis, the purpose of the book being of a wholly different character, and, furthermore, because these theories have been exhaustively treated in a masterly manner in special volumes readily accessible to all students of chemistry.

The present edition differs greatly from its predecessors. Among the very first changes will be observed the de-

scription of an electro-chemical laboratory. This laboratory has been the outgrowth of a real demand and cannot fail to be suggestive and perhaps helpful to persons who purpose making an installation for electrolytic work. A few alterations have been made in the historical section, but the great changes will appear in the sections devoted to the determination and separation of the metals. Many of the earlier directions in reference to the determination of the individual metals have been omitted and more reliable and definite conditions substituted for the same. The section devoted to separations has been entirely recast, each separation being given in all of its possible forms with conditions that experience has demonstrated will yield satisfactory results.

The new illustrations scattered here and there through the text have been made from photographs taken by Mr. Walter T. Taggart, Sc.B., to whom the author's thanks are here expressed. It is also a great pleasure to acknowledge indebtedness to the many students who, through a period of years, have with readiness and skill tested methods of determination and separation, time after time, as the writer has suggested.

S.

THE JOHN HARRISON LABORATORY
OF CHEMISTRY,
1902.

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ABBREVIATIONS.

AM. CH.	—	<i>The American Chemist.</i>
AM. CH. JR.	—	<i>American Chemical Journal.</i>
AM. JR. SC. AND AR.	—	<i>American Journal of Science and Arts.</i>
AM. PHIL. SOC. PR.	—	<i>Proceedings of the American Philosophical Society.</i>
ANN.	—	<i>Annalen der Chemie und Pharmacie.</i>
BER.	—	<i>Berichte der deutschen chemischen Gesellschaft.</i>
BERG. HÜTT. Z.	—	<i>Berg- und Hüttenmännische Zeitung.</i>
B. S. CH. PARIS	—	<i>Bulletin de la Société Chimique de Paris.</i>
CH. NEWS	—	<i>Chemical News.</i>
CH. Z.	—	<i>Chemiker-Zeitung.</i>
C. R.	—	<i>Comptes Rendus.</i>
DING. P. JR.	—	<i>Dingler's Polytechnisches Journal.</i>
ELEKTROCH. Z.	—	<i>Elektrochemische Zeitschrift.</i>
G. CH. ITAL.	—	<i>Gazzetta chimica italiana.</i>
JAHRB.	—	<i>Jahresbericht der Chemie.</i>
J. AM. CH. S.	—	<i>Journal of the American Chemical Society.</i>
JR. AN. CH.	—	<i>Journal of Analytical and Applied Chemistry.</i>
JR. F. PRT. CH.	—	<i>Journal für praktische Chemie.</i>
JR. FR. INS.	—	<i>Journal of the Franklin Institute, Phila.</i>
M. F. CH.	—	<i>Monatshelt für Chemie.</i>
PHIL. MAG.	—	<i>Philosophical Magazine.</i>
WIED. ANN.	—	<i>Wiedemann's Annalen.</i>
Z. F. A. CH.	—	<i>Zeitschrift für analytische Chemie.</i>
Z. F. ANG. CH.	—	<i>Zeitschrift für angewandte Chemie.</i>
Z. F. ANORG. CH.	—	<i>Zeitschrift für anorganische Chemie.</i>
Z. F. ELEKTROCHEM.	—	<i>Zeitschrift für Elektrochemie.</i>
Z. F. PH. CH.	—	<i>Zeitschrift für physikalische Chemie.</i>

ELECTRO-CHEMICAL ANALYSIS.

INTRODUCTION.

Many chemical compounds are decomposed when exposed to the action of an electric current. A decomposition of this kind is called *electrolysis*, while the substance undergoing change is termed an *electrolyte*. The products of the decomposition are the *anions* and *cations*, or those (1) which separate at the *anode*, the positive electrode or pole (+ P), and (2) those separating at the *cathode*, the negative electrode or pole (— P) of the source of the electric energy.

This behavior of compounds has become of great service to the analyst, inasmuch as it has enabled him to effect the isolation of metals from their solutions, and by carefully studying the electrolytic behavior of salts it has been possible for him to bring about quantitative determinations and separations.

The electrolytic method of analysis is especially inviting, since it permits of clean, accurate, and rapid determinations where the ordinary methods yield unsatisfactory results. This statement is readily confirmed on recalling the gravimetric methods usually employed in the estimation of copper, mercury, cadmium, bismuth, tin, etc., etc. That this assertion may be the conviction