

**INSTRUMENTAL METHODS
FOR
ANALYSIS
OF
SOILS
AND
PLANT TISSUE**

INSTRUMENTAL METHODS FOR ANALYSIS OF SOILS AND PLANT TISSUE

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**Soil Science Society of America, Inc.
Madison, Wisconsin USA**

1971

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Soil Science Society of America, Inc.
677 South Segoe Road
Madison, Wisconsin 53711

Library of Congress Catalog Card Number: 77-154109

FOREWORD

Due to the many recent technological advances directly applicable to analyses of soil and plants, "Instrumental Methods for Analysis of Soils and Plant Tissue" is a very timely and appropriate symposium topic. New instruments have recently been developed; we are now seeing improvements and additional applications for instruments in use for several years. Atomic absorption spectrophotometry and ion-specific electrodes are among the recent developments which are bringing about nearly revolutionary changes in plant and soil analysis. The development of the electron microprobe and its application to study of soil samples have enabled us to "see" and understand soils as never before. Gas chromatography and fluorometry have greatly extended the range of our analyses. Their development has added useful tools, especially in our studies of potential pollutants in waters, which may have originated from soils. The role of other instruments, such as neutron activation analysis, is yet to be fully researched or exploited. Automation techniques plus new sample extraction and preparation procedures are allowing more effective use of our instruments. Recently we have seen greater interest in and more use made of plant tissue analysis.

Instrumental analyses are now conducted for purposes other than diagnosis of nutrient deficiencies and soil fertility evaluation, such as determination of content of potential pollutants and study of plant nutrient uptake and metabolic processes.

All of these developments demonstrate the increased importance and complexity of instrumental analysis. The Soil Science Society of America is thus pleased to present this publication as an aid to a better understanding of the use and role of instruments in soil and plant analysis. The society is grateful to Dr. Leo M. Walsh, chairman of the organizing committee for the symposium and also chairman of the editorial committee for this publication, for the time and effort he has devoted to this activity. We also express our appreciation to the participants in the symposium and contributors to chapters of this publication.

February 1971

Ralph J. McCracken, President
Soil Science Society of America

PREFACE

All but three of the papers in this publication were originally presented at an invitational symposium on Instrumental Methods for Analysis of Soils and Plant Tissue during the 1970 annual meeting of the Soil Science Society of America at Tucson, Arizona, August 23-28. The papers by R. L. Flannery and D. K. Markus and J. Kubota and V. A. Lazar were originally published in Part I and Part II, respectively, of SSSA Special Publication No. 2, Soil Testing & Plant Analysis, and were revised for inclusion in this publication. The paper by J. E. Steckel and R. L. Flannery was not previously published or presented at a symposium; however, it is included here because autoanalysis is an important method of analyzing plant tissue.

The objective of this publication was to compile a series of papers covering the techniques and uses of various instrumental methods for analyzing soil, plant tissue, and water. The methods discussed include many of those presently used in routine analytical laboratories, as well as a number of relatively new instrumental techniques which may be used routinely in the future. Recent developments in instrumentation are now, or likely will be, very useful for analysis of potential pollutants and for study of nutrient movement and metabolic processes within the plant.

This publication should prove to be very useful for research scientists, supervisors of analytical laboratories, and extension agronomists. Also, students in advanced courses in soil chemistry and plant nutrition should find the book a valuable reference.

The 1970 Committee on Soil Testing and Plant Analysis (S-877) was charged with the responsibility of organizing the 1970 symposium and compiling this publication. The committee wishes to express appreciation to the program chairmen of the divisions co-sponsoring the symposium (S-2, Dr. D. H. Brown; S-4, Dr. W. H. Schmehl; S-8, Dr. R. D. Munson; and C-2, Dr. C. A. Hanson), to Dr. C. I. Rich, immediate past president of SSSA, and to Dr. R. J. McCracken, president of SSSA, for their help and advice in accomplishing this work. Dr. J. B. Jones is also acknowledged for the early encouragement he provided. Finally, the

committee is indebted to the headquarters staff of ASA for their assistance in organizing the symposium and compiling this publication

February 1971

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Conversion Factors for English and Metric Units and Plant Nutrients

To convert column 1 into column 2, multiply by	Column 1	Column 2	To convert column 2 into column 1, multiply by
LENGTH			
0.621	kilometer, km	mile, mi	1.609
1.094	meter, m	yard, yd	0.914
0.394	centimeter, cm	inch, in	2.54
AREA			
0.386	kilometer ² , km ²	mile ² , mi ²	2.590
247.1	kilometer ² , km ²	acre, acre	0.00405
2.471	hectare, ha	acre, acre	0.405
VOLUME			
0.00973	meter ³ , m ³	acre-inch	102.8
3.332	hectoliter, hl	cubic foot, ft ³	0.2832
2.838	hectoliter, hl	bushel, bu	0.352
0.0284	liter	bushel, bu	35.24
1.057	liter	quart (liquid), qt	0.946
MASS			
1.102	ton(metric)	ton (English)	0.9072
2.205	quintal, q	hundredweight, cwt (short)	0.454
2.205	kilogram, kg	pound, lb	0.454
0.035	gram, g	ounce (avdp), oz	28.35
PRESSURE			
14.50	bar	lb/inch ² , psi	0.06895
0.9869	bar	atmosphere,* atm	1.013
0.9678	kg (weight)/cm ²	atmosphere,* atm	1.033
14.22	kg (weight)/cm ²	lb/inch ² , psi	0.07031
14.70	atmosphere,* atm	lb/inch ² , psi	0.06805
YIELD OR RATE			
0.446	ton(metric)/hectare	ton (English)/acre	2.240
0.891	kg/ha	lb/acre	1.12
0.891	quintal/hectare	hundredweight/acre	1.12
1.15	hectoliter/ha, hl/ha	bu/acre	0.87
TEMPERATURE			
$(\frac{9}{5}^{\circ}\text{C}) + 32$	Celsius	Fahrenheit	$\frac{5}{9} (^{\circ}\text{F} - 32)$
-17.8 C		0 F	
0 C		32 F	
20 C		68 F	
100 C		212 F	

PLANT NUTRITION CONVERSION--P AND K

$$\text{P (phosphorus)} \times 2.29 = \text{P}_2\text{O}_5$$

$$\text{K (potassium)} \times 1.20 = \text{K}_2\text{O}$$

* The size of an "atmosphere" may be specified in either metric or English units.

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Use of Automated Combustion Techniques for Total Carbon, Total Nitrogen, and Total Sulfur Analysis of Soils¹

J. M. BREMNER and M. A. TABATABAI²

Dry combustion techniques have not been used extensively for total carbon, total nitrogen, or total sulfur analysis of soils, because the techniques available have been complicated and time-consuming compared with wet oxidation methods and have not been suitable for routine analysis of soils. These defects of dry combustion methods of analysis have largely been overcome by the recent development of automated combustion techniques that are very simple and rapid compared with previous techniques. The purpose of this paper is to describe automated combustion instruments that have been evaluated for determination of total carbon, total nitrogen, and total sulfur in soils and to summarize current information concerning use of these instruments for soil analysis.

Correspondence with manufacturers of automated combustion instruments during preparation of this paper showed that several instruments besides those discussed here have been used to analyze soils, but no work to evaluate these instruments for soil analysis has been reported. Also, the manufacturers' specifications indicate that most of these instruments are designed for analysis of pure compounds or homogeneous materials having high carbon, nitrogen, or sulfur contents and are not suitable for analysis of soils or other heterogeneous materials with low contents of these elements.

¹ Journal Paper no. J-6685 of the Iowa Agriculture & Home Economics Experiment Station, Ames, Iowa. Project no. 1835.

² Professor and Research Associate, respectively, Department of Agronomy, Iowa State University, Ames, Iowa.

TOTAL CARBON

The only automated combustion instrument evaluated for total carbon analysis of soils is the Leco 70-Second Carbon Analyzer supplied by the Laboratory Equipment Corp., St. Joseph, Mich. This instrument was designed for total carbon analysis of iron and steel, but its speed and simplicity make it very attractive for analysis of nonferrous as well as ferrous materials, and recent work (26) has shown that it is readily adaptable for determination of total carbon in soils.

The Leco 70-Second Carbon Analyzer consists of an oxygen-purification train, a high-frequency induction furnace, and a carbon dioxide determinator that utilizes the difference in thermal conductivity between carbon dioxide and oxygen. In total carbon analysis by this instrument, the sample is treated in a ceramic crucible with combustion accelerators (usually iron plus tin and tin-coated copper) and heated to high temperature (above 1,650C) in a stream of purified oxygen, the high temperature being generated by using an induction furnace to induce an electrical field in the accelerator-treated sample. The gases evolved are passed through a dust trap (to remove metal oxides), a trap containing activated manganese dioxide (to remove sulfur oxides, nitrogen oxides, and halogen gases), a heated catalyst (hopcalite) tube (to convert CO to CO₂), and a trap containing anhydrous magnesium perchlorate (to remove water vapor). The purified CO₂-O₂ mixture thus obtained is collected in a cylinder maintained at a constant temperature (45C) and is analyzed for CO₂ by measuring its thermal conductivity with a thermistor-type thermal conductivity cell. The gas collection cylinder is housed in an oven above ambient temperature to eliminate extraneous temperature variations that would cause an imbalance in the thermal conductivity cell. The output of the thermal conductivity cell is amplified by a DC amplifier, and the output of the amplifier is recorded automatically as milligrams of carbon on a digital meter. The thermal conductivity cell is balanced so that, with pure oxygen in the cylinder, it gives zero output on the digital meter. With the instrument thus balanced, the output of the cell as measured on the meter is proportional to the amount of CO₂ in the cylinder. This thermal-conductivity technique has important advantages over previous methods of determining CO₂, and the entire analysis procedure is rapid and simple. The analyzer functions automatically once the accelerator-treated sample is placed in the induction furnace and the cycle switch is pressed to initiate the sequence of operations. Before use, the analyzer is calibrated with carbon standards. The metallic-carbon standards supplied by the Laboratory Equipment Corp. are convenient for this purpose.

Figure 1 and Table 1 show results obtained in work to evaluate the Leco 70-Second Carbon Analyzer for total carbon analysis of

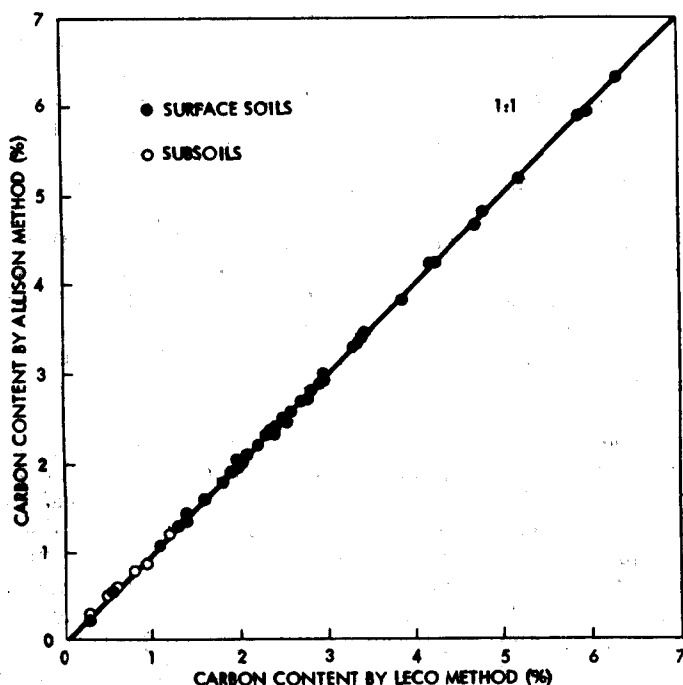


Fig. 1—Results of total carbon analysis of 46 soils by Leco 70-Second Carbon Analyzer versus results by Allison method (26)

Table 1 — Comparison of results obtained in total carbon analysis of soils by Leco 70-Second Carbon Analyzer and by wet combustion method of Allison (26)

Soil	Method*	No. of analyses	Total C content, %†	
			Mean	SD
Buckner	L	8	0.32	0.02
	A	5	0.31	0.02
Ida	L	8	1.10	0.02
	A	6	1.15	0.03
Hayden	L	8	3.06	0.02
	A	6	3.07	0.02
Oxbow‡	L	5	3.36	0.03
	A	5	3.38	0.03
Glencoe	L	8	8.80	0.13
	A	6	8.67	0.13
Peat	L	5	34.2	0.25
	A	5	33.5	0.90

* L, Leco C Analyzer; A, Allison method (1).

† Five analyses. SD, standard deviation.

‡ 26.5% CaCO₃.

soils (26). The 46 soils used in this evaluation were selected so that they differed markedly in organic-matter content (0.3-34% organic C), texture (2-94% sand, 1-43% clay), and carbonate content (0-26.5% CaCO_3), and the total carbon values obtained in analysis of these soils by the Leco Analyzer were compared with those obtained by the wet combustion method of Allison (1), which has gained acceptance as a reliable method of determining total carbon in soils. The data reported show that the total carbon values obtained by the Leco Carbon Analyzer agreed closely with those obtained by Allison's method and that the Leco method of analysis was at least as precise as Allison's method. Other studies performed in the work quoted showed that the Leco 70-Second Carbon Analyzer gives quantitative recovery of carbonate-C and that the results of soil analysis by this instrument are not affected by the presence of substantial amounts of chloride. A study of the effect of sample mesh-size on total carbon analysis of mineral soils by the Leco Analyzer showed that the precision of the results obtained with this instrument usually increased with a decrease in soil mesh-size but that, with most soils studied, the results with <40-mesh soil were almost as precise as those obtained with <100-mesh or <300-mesh soil (Table 2). Soil samples containing 2-10 mg of carbon (usually 0.2-0.3 g of mineral soil) were found satisfactory for total carbon analysis by the Leco Analyzer. With several soils, incomplete combustion was observed when the amount of soil taken for analysis exceeded 0.5 g or contained more than 12 mg of carbon.

Total carbon analysis of soils with the Leco 70-Second Carbon Analyzer is very simple and rapid, and a single operator can easily perform more than 150 analyses in a normal working day (including weighing of soil samples). Well over 250 analyses of preweighed samples can be performed within 8 hours.

Preliminary work in our laboratory indicates that the Leco Carbon Analyzer can be used satisfactorily for determination of

Table 2 — Effect of sample mesh-size on total carbon analysis of soils by Leco 70-Second Carbon Analyzer (26)

Soil	Sample mesh-size	Total C content by Leco Analyzer, %*	
		Mean	SD
Lindley	10	1.29	0.11
	40	1.33	0.03
	100	1.36	0.01
Sharpsburg	10	2.36	0.06
	40	2.31	0.02
	100	2.29	0.02
	300	2.28	0.01
Grundy	10	2.63	0.04
	40	2.68	0.04
	100	2.66	0.03
	300	2.64	0.03

* Five analyses. SD, standard deviation.

organic carbon in soils and soil extracts if the sample is pretreated with dilute HCl to remove carbonate-C and subsequently dried before analysis.

Morris and Schnitzer (20) have used an Aminco C and H Analyzer (American Instrument Co., Inc., Silver Spring, Md.) with automatic readout of CO₂ for determination of carbon in soil extracts, but no evaluation of this instrument for soil analysis has been reported.

TOTAL NITROGEN

The only automated combustion instruments thus far evaluated for total nitrogen analysis of soils are the Nitrogen Analyzers supplied by Coleman Instruments, Inc., Maywood, Ill. These analyzers are automated Dumas combustion instruments, and three models are available (see Table 3 for specifications).

The original Coleman Nitrogen Analyzer (Model 29) is an automatic micro-Dumas apparatus that corresponds very closely to the prototype designed and described by Gustin (11). In total nitrogen analysis with this instrument, the sample is mixed with combustion catalyst (usually CuO) and heated to above 900C in a quartz combustion tube filled with catalyst. This heating to pyrolyze the sample is carried out in an atmosphere of high-purity CO₂, and the gases evolved are swept by purified CO₂ through a post-heater tube containing Cu in the first half of its length and CuO in its terminal section. This tube is heated by an auxiliary furnace (usually to 600-700C), and its function is to reduce oxides of nitrogen to N₂, oxidize any H₂ to H₂O, and convert CO to CO₂. The gas stream from the post-heater tube passes into a glass nitrometer containing concentrated alkali (KOH solution), where it is released from a nozzle under mercury in the form of a stream of small bubbles. These bubbles are brought into contact with the alkali by a magnetic stirrer, which ensures complete absorption of CO₂, and the N₂ collects in the body of the nitrometer, displacing alkali into a reservoir. The N₂ in the nitrometer is then measured volumetrically by drawing it into a precisely calibrated stainless steel syringe. The

Table 3 — Coleman Nitrogen Analyzers (manufacturer's specifications)

Specification	Analyzer model		
	29	29A	29B
Sample size, mg	2-50	25-500	2-500
Maximal amount of N in sample, mg	4	40	4
Capacity of nitrometer syringe, ml	5	50	5
Reproducibility of nitrometer syringe, μ liters	± 2	± 10	± 2
Operating cycle, min	8	12	12
Readout	Digital counter	Motor-driven digital counter	Digital counter
Number of analyses per hour	4-5	3-4	3-4