

Elemental C, H and N Microanalysis of Crushed Rock and Soil Samples¹

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ABSTRACT

A sensitive and reproducible method for elemental analysis of rock and soil samples has been developed using a modified Hewlett-Packard 185 CHN analyzer. Samples are combusted in an inert He atmosphere (with and without catalyst) with a carefully controlled combustion time and temperature. Absolute mass calibration is available on samples of from 1-500 μg total CHN content. Analysis of chromatograms is made by both manual and computer techniques. Finely crushed rock (or dust) samples of from 50-100 mg may be analyzed for most forms of carbon content and for N and H with a high degree of technical reproducibility. Step-wise calcination at 150 C and 550 C allows evaluation of adsorbed CO_2 , potential organic and amorphous carbon content. Although carbide carbon is partially recovered, essentially quantitative recovery of finely divided graphitic (and diamond) as well as amorphous, carbonate and all organic carbon may be obtained.

INTRODUCTION

For many decades elemental analysis by the classic

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techniques of Pregl for C and H and Dumont for N have been the ultimate standard and criteria for purity in organic microanalysis (1). The traditional apparatus and procedures placed unusual and severe technical demands upon the analyst. However with the introduction of the semiautomated CHN analyzers a few years ago, the ease and rapidity of analysis suddenly improved. Such improved elemental analytical procedures have been reviewed and compared by Salzer (2). Under optimum conditions essentially equivalent results may be obtained by such CHN analyzers as compared with the classical techniques (3). Although normally applied to organic microanalysis, this CHN technique with modifications can be applied to the analysis of crushed rock and soil samples of small particle size. Extremely low levels of C, H and N may be measured. Further some discrimination with regard to the presence of organic, carbonate, amorphous, graphitic (or diamond) and carbide carbon may be made.

METHODS AND MATERIALS

All elemental analyses were made on a modified Model 185 CHN analyzer equipped with an HP-18 helium purifier (Hewlett-Packard, Palo Alto, Calif.). To permit absolute mass calibration the automatic attenuator and coupling with the Cahn Gram-O-matic balance was disconnected.

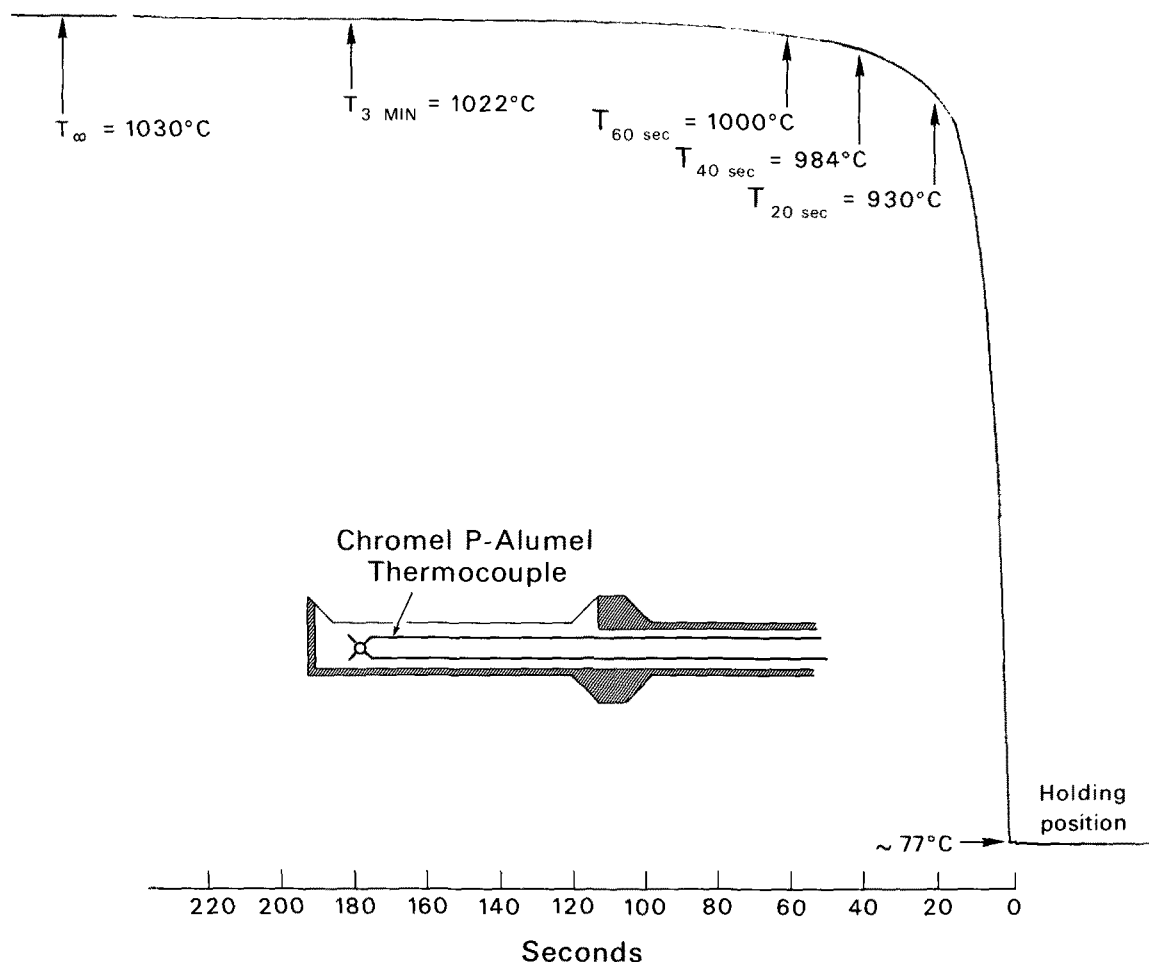


FIG. 1. Profile of thermal rise in the injection rod cavity.

Recorder performance was monitored and results insured on all samples by feeding the thermal conductivity detector output to two independently attenuated 1 mV strip chart recorders (Model V-16, Minneapolis Honeywell, Minneapolis, Minn.). Line voltage to all critical components was stabilized using a Sorensen voltage regulator.

Certain apparatus modifications were required to improve performance and to achieve needed stability at maximum sensitivity. Some of these have been presented earlier (4), and those utilized here are as follows: a dual channel 12 hr cycling H₂O-glycerol humidifier, permitting higher humidification during the night and lower during the day's running period; a finer zeroing potentiometer; an ammeter for the furnace circuit to reproducibly set the furnace variac; a foot switch with a precision timer to exactly time (and to vary precisely) the furnace combustion (and bypass) cycle; the column fan motor is disconnected to avoid noise; a silicone rubber injection rod gasket is substituted for the viton gasket; and a close fitting quartz sleeve is installed on the Hastelloy "X" oxidation furnace tube to prolong life and to eliminate irregular tube sag. Also a calibrated chromel-alumel thermocouple monitor is provided with options for monitoring either outside or inside the oxidation furnace. The latter monitor consisted of a thermocouple embedded in a specially fabricated injection rod permitting measurement of the temperature

TABLE I

Evaluation of Errors, Low Level Carbon Analysis

Quantified errors	Unquantified random errors
Injection rods, duplicate pairs Operator 1 (GRS) n = 61, $\sigma_{SEM} = \pm 0.100 \mu\text{g C}$ Operator 2 (FTL) n = 22, $\sigma_{SEM} = \pm 0.109 \mu\text{g C}$ Injection rods + 30-35 mg catalyst, all run the same day Operator 1 and 2n = 10, $\sigma_{SEM} = \pm 0.184 \mu\text{g C}$ CaCO ₃ calibration, 15-21 μg carbon (125-175 μg CaCO ₃), duplicate pairs Operator 1 (GRS) n = 25, $\sigma_{SEM} = \pm 0.193 \mu\text{g C}$ Operator 2 (FTL) n = 7, $\sigma_{SEM} = \pm 0.196 \mu\text{g C}$	Manipulation of sample, sampling statistics and associated problems, in- cluding "coning effect," i.e., segregation of large from small particles and segregation of denser from lighter particles of similar size. Contamination (sample containers, dust fallout, gasket scrape, etc.).

rise within the sample cavity (as a function of time) during typical combustion cycles.

Analysis of chromatograms was by either manual or computer processing of the data. The manual procedure for carbon alone assumed mass linearity of the peak height-

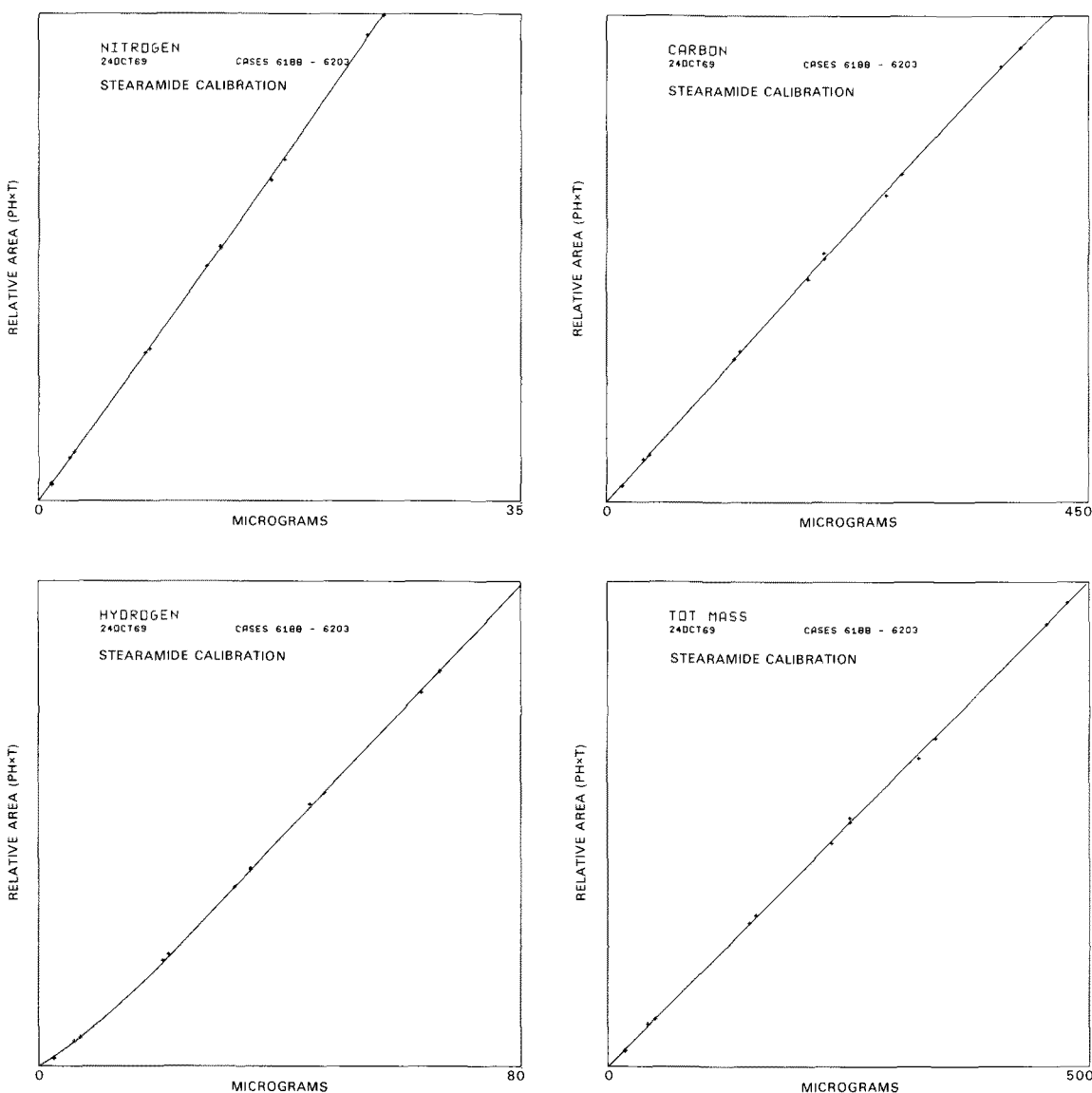


FIG. 2. Calibration curves for N, C, H and total mass obtained over the range of 20-500 μg stearamide.

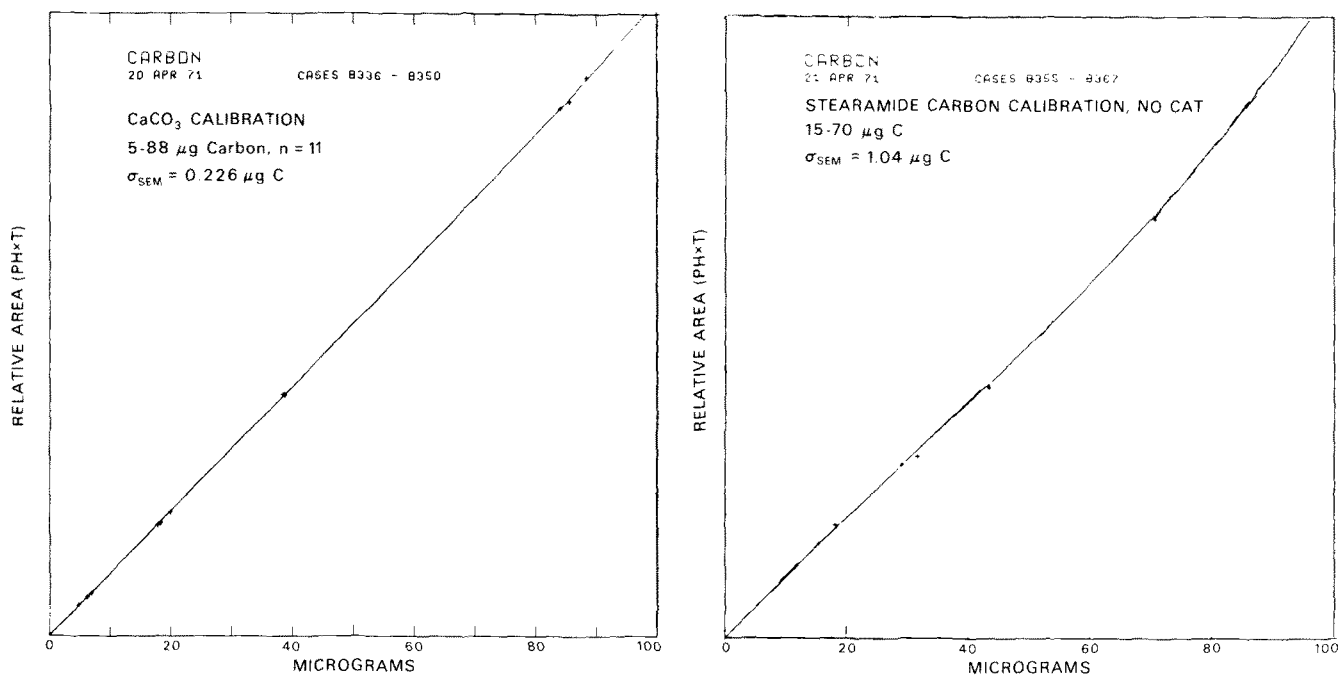


FIG. 3. Low level carbon calibration of CaCO_3 and stearamide, no catalyst (CAT).

background measurements. For CHN measurements a computer sequence, using peak height \times effective elution time as a parameter, for each element was employed as described earlier (4). All such data were processed at the Lawrence Berkeley Laboratory Computer Center using a Control Data

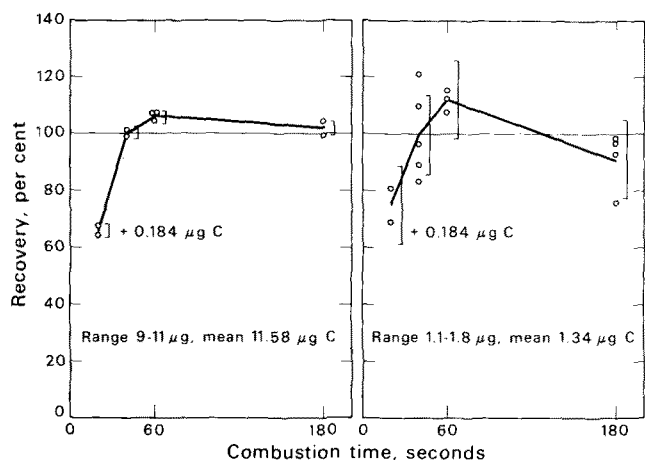


FIG. 4. Graphitic carbon recovery with the catalyst as matrix.

Corporation 6600 computer. A primary absolute mass calibration over the dynamic range (20-500 μg) of the instrument was made for C, H and N, using weighed standard samples of stearamide with 35-40 mg catalyst ($\text{MnO}_2 + \text{WO}_3$). Best fit third order polynomials were fitted to the three components. Normally daily calibration involved the use of a calcined (550 C) CaCO_3 standard (130-150 μg) or 350 μg methyl stearate samples. The former were weighed in Hewlett-Packard 5080-5045 boats and emptied into the injection rod cavity without catalyst.

Using the daily calibration values, the primary calibration polynomials were rotated so the curves fell on the mean point or points measured. At levels of 15-18 μg carbon (as carbonate) fluctuations in absolute carbon mass calibration were consistently less than $\pm 2\%$ over the experimental period reported here, whether measured before or after the sample analyses. Standards calcined at 550 C included amorphous CaCO_3 , -325 mesh graphite (C-001), -325 mesh Cr_3C_2 (CR-11) (Research Organic/Inorganic Chemical Corp., Sun Valley, Calif.), and synthetic diamond ultra fines (General Electric Co., Worthington, Ohio). Other standards used were argillaceous limestone (Standard Reference Material 1b, National Bureau of Standards) and calcite crystal. A sample of crushed Sierra Nevada Latite was used for direct study and, after 7%

TABLE II

Recovery of Amorphous Carbon, Lamp Black 245 C^{a,b}

Sample	LT (550 C) No CAT, ^b ppm	LT + CAT, ppm	LT + LB No CAT, μg	LT + LB CAT, μg
	12.3	15.3		
	10.2	15.4		
Amount expected from LT		0.85		1.20
		0.76		1.05
Mass LB added		21.3		21.2
		13.4		18.9
Mass C found		1.22		22.69
		0.97		19.62
ΔLB to chromatogram		0.37 (1.7% recovery)		21.5 (+ 0.3)
		0.21 (1.6% recovery)		18.6 (- 0.3)

^a CaCO_3 calibration, 22.50 μg C, 1 mV full scale (no attenuation), manual calculations.

^bLT = Latite-TiO₂; CAT = catalyst; LB = lamp black.

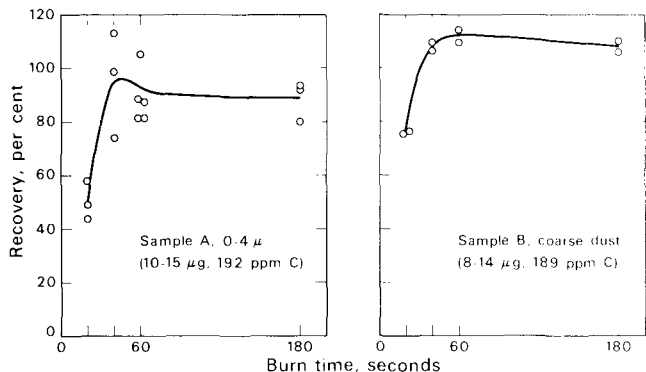


FIG. 5. Synthetic diamond dust recovered in the catalyst matrix. Coarse dust was -325 mesh.

enrichment with TiO₂ and calcination (550 C), was utilized as a low level standard and matrix.

To allow adequate packing of 50-100 mg crushed rock specimen (without loss) plus approximately 40 mg catalyst, it was found necessary to use the older style injection rods (F & M No. 2-5554). Although Perkin-Elmer boats (29-410 M) and Hewlett-Packard 5080-5045 boat caps were used for the primary calibration, to minimize background daily CaCO₃ calibration and the crushed rock samples were placed directly in the injection rod cavity.

Samples were combusted in an inert He atmosphere with and without catalyst. At an oxidation furnace setting of 1065 C the 20 sec thermal rise within the cavity was 930 C, although some additional combustion continued after the furnace flow mode was resumed. These combustion conditions, without catalyst, gave quantitative recovery of carbonate carbon and at low levels (less than 100 μg) most organic carbon. Amorphous carbon and higher levels of organics required catalyst. A complete profile of temperature with time is shown in Figure 1. Longer burn times than 20 sec with catalyst allowed essentially quantitative recovery of both graphitic and diamond fines, but only partial recovery of carbide carbon.

RESULTS AND DISCUSSION

Table I shows the stability of the instrument with respect to injection rod background, porcelain mortared and calcined (550 C) catalyst and the daily CaCO₃ calibrations. Also potential sources of random error in

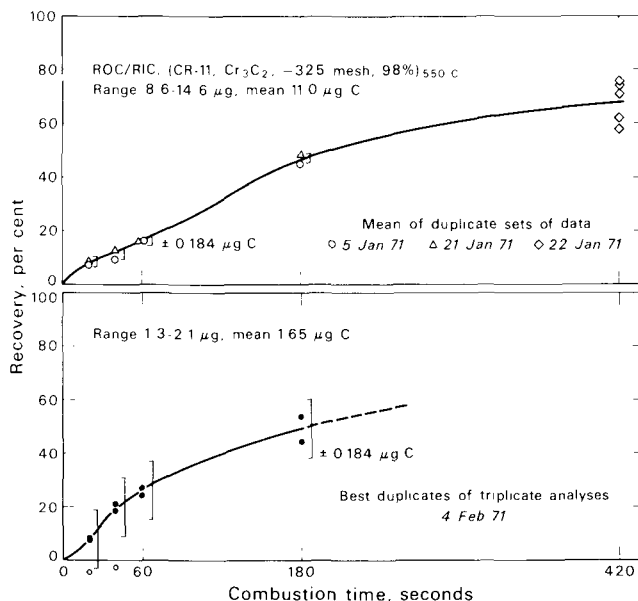


FIG. 6. Chromium carbide recovery in the catalyst as matrix.

sample analysis are given.

The results of a complete stearamide calibration for N, C, H and total mass are given in Figure 2. However since many analyses involved small amounts of carbon, a lower level calibration was needed. Figure 3 shows a CaCO₃ calibration demonstrating linearity over the range of 5-90 μg C. A similar calibration curve is obtained over the same range of carbon for stearamide without catalyst, illustrating quantitative recovery at such levels of carbon. Weighing errors account for the significant difference in the standard error of measurement values for the two sets of data.

The recovery of amorphous carbon at a level of 20 μg was tested with and without catalyst. Table II shows approximately 2% recovery without catalyst and with catalyst essentially 100% recovery (considering the error of weighing).

Idealized recovery of graphitic, diamond and intermediate type carbide carbon was evaluated using the catalyst as a matrix. This was done to eliminate the large error inherent in using a matrix such as the crushed latite. (The weighed carbon and catalyst were mortared under nearly dust-free conditions.) To evaluate this recovery it

TABLE III

A. Recovery (ppm) of Carbon in Raw Latite, Latite-TiO ₂ and CaCO ₃ Content of Argillaceous Limestone ^a				
(Raw Latite)	(Latite-TiO ₂) 550 C		(Argillaceous Limestone) ^b	
29 Sept 70	22 Sept 70	25 Sept 70	22 Sept 70	18 Mar 70
450,395	11.6	11.9	93.29% (18.47)	93.33% (271.6)
356,331	13.0	11.3	92.47% (17.51)	92.48% (305.2)
	11.2	11.3		

^aManual calculations (μg C analyzed in parentheses).
^bStandard reference material 1b, 110 C, 2 hr (91.3%, CaCO₃). Wt% values given assume all carbon as carbonate.

B. Recovery (ppm) of Forms of Added Carbonate to (Latite-TiO ₂) _{550 C} Matrix, Porcelain Mortared ^a 25 Sept 70		
Σ 201.3 ppm	Σ 201.6 ppm	Σ 201.7 ppm
(L-TiO) _{550 C} + (CaCO ₃) _{550 C}	(L-TiO) _{550 C} + (Aragonite) _{110 C}	(L-TiO) _{550 C} + Calcite
206.0 (13.40)	203.9 (13.59)	196.4 (11.66)
205.0 (11.33)	206.2 (13.30)	198.6 (13.16)

^aManual calculations (μg C analyzed in parentheses). Calcite was not calcined.

TABLE IV

Recovery (ppm), Mixed Carbon Standard
120 ppm (CaCO₃) + 30 ppm (EDTA) Carbon + (Latite)_{550 C} Matrix

9 August 70	11 August 70	12 August 70	14 August 70	15 August 70	(Parent latite) _{550 C}
(Parent latite) _{550 C}	MCS ^a	MCS	MCS	MCS	(Parent latite) _{550 C}
8.0 (1.03)	167.2 (8.05)	160.0 (6.22)	159.2 (9.57)	175.0 ^b (7.40)	6.6 (0.72)
8.4 (1.03)	166.6 (9.64)	161.0 (6.59)	175.1 ^b (12.96)	175.2 ^b (10.17)	6.6 (0.73)
6.4 (0.63)	160.8 (10.26)		160.6 (10.20)	161.5 (8.70)	
6.6 (0.58)	169.2 (6.86)			161.6 (9.50)	
CaCO ₃ standard (μg C, 1 mV full scale)					
22.51		22.01	22.24	22.66	
22.22		21.61	21.77	22.20	

^aMCS = Mixed carbon standard.

^bProbable contamination. (μg C analyzed in parentheses), manual calculations, no catalyst.

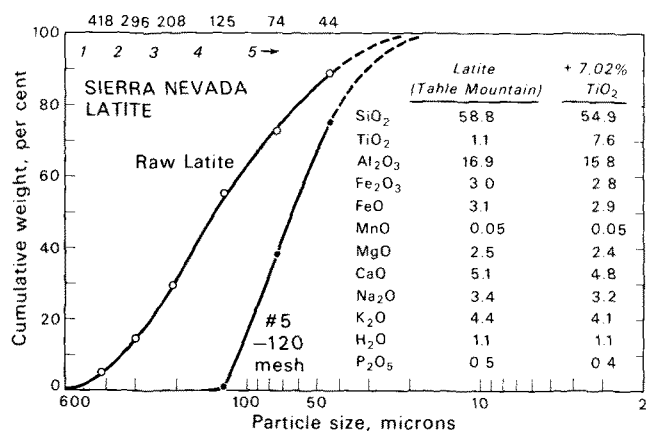


FIG. 7. Particle size distribution and approximate chemical composition of the raw latite and the matrix.

was also necessary to run a profile of burn times from 20 sec to as much as 7 min. The data in Figures 4 and 5 demonstrate essentially quantitative recovery at 40 sec in this system for small particle-size graphitic carbon and diamond at the 1 and 10 μg levels, and 10 μg level, respectively. However the recovery of Cr₃C₂ shown in Figure 6 illustrates a unique profile of partial recovery. Again such reproducible partial recovery was demonstrated at both the 1 and 10 μg levels of total carbide carbon.

Since much of the carbon present in terrestrial rock and soil samples is in the form of carbonate and organic carbon, the recovery of these forms at a level of 200 ppm in a calcined latite-TiO₂ matrix was tested. Standard 20 sec burn times were used and no catalyst employed. Table IIIA and B show quantitative recovery of amorphous, aragonite (argillaceous limestone) and calcite forms of carbonate. Table IV shows the recovery of a combined CaCO₃ and organic standard in the calcined latite matrix. Again

TABLE V

Raw Latite, Sample I, Carbon Recovery (ppm), Particle Size Effect^a

Fraction (μ size)	Wt %	Burn times 20 sec	Burn times 20 sec
No. 1 (418 < d)	4.8	248 (260) 390 (111) 95 (184) 627	Σ ₁ ⁵ Whole crush 325 (571) 326 (544) (414)
No. 2 (296 < d < 418)	9.5	164 (188) 101 (271) 137	Σ ₁ ⁵ C _i x wt% = 341 (435) 100
No. 3 (209 < d < 296)	15.5	150 (150) 157 (189)	Burn times
No. 4 (125 < d < 209)	25.7	216 (251) 208 (276)	40 sec 60 sec 180 sec
No. 5 (d < 125)	44.5	508 (684) 539 (712)	632 (860) 661 (982) 745 (950) 638 (919) 696 (953) 767 (922)

^aSample mass 64-142 mg, (12-98 μg C), manual calculations (values with catalyst in parentheses).

TABLE VI

Raw Latite, Sample II, Carbon Recovery (ppm), Particle Size Normalization^a

Sample, μ size)	Burn times				
	20 Sec	20 Sec ^b	40 Sec ^b	60 Sec ^b	180 Sec ^b
No. 2 (296 < d < 418)	115	292 (296)	(300)	(320)	(326)
No. 3 (209 < d < 296)	142	282 (290)	(310)	(324)	(310)
No. 4 (125 < d < 209)	209	254 (277)	(296)	(286)	(285)
No. 5 (d < 125)	151	250 (293)	(292)	(324)	(278)
	219	353 (385)	(454)	(452)	(417)
	233	340 (410)	(437)	(442)	(396)
	536 (704)		(984)	(1023)	(1000)
	580 (724)		(1008)	(1003)	(1000)
	536 (758)				
	572 (756)				
Σ ₁ ⁵ whole crush	450 331				
	356 395				

^aSample mass 48-128 mg (16-93 μg C). Manual calculations (values with catalyst in parentheses).

^bFractions 2-4 are normalized to d < 125 μ.

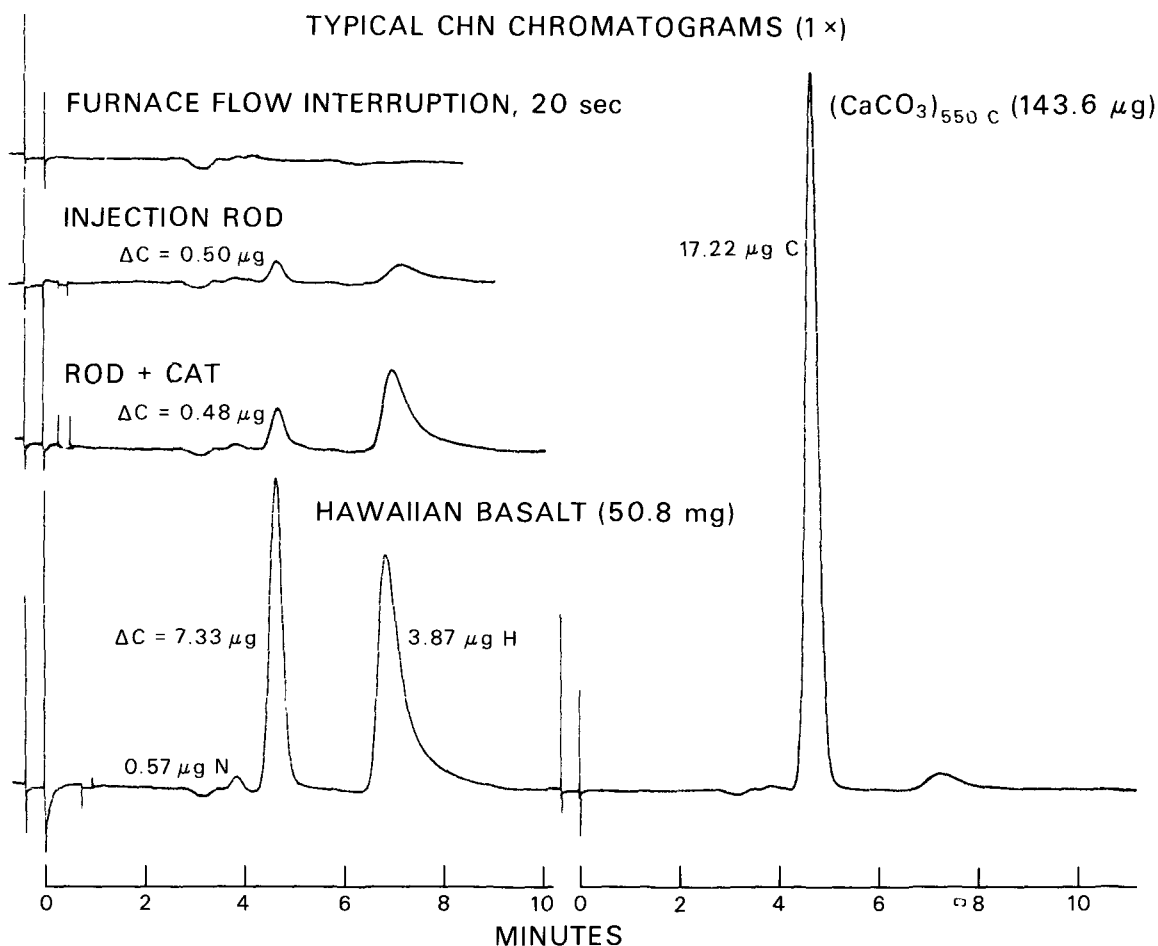


FIG. 8. Typical CHN chromatograms showing increments of carbon analyzed (all at maximum sensitivity, 1 mV full scale).

reproducible quantitative recovery is achieved at approximately the 10 μg level of total carbon. All the higher values represent probable contamination, reflecting the limitations of the method by various random errors, discussed earlier.

Some detailed analysis of the raw latite sample itself was made. The particle size distribution (by dry sieving) and approximate chemical composition (5) of this sample are given in Figure 7. The effect of particle size on the amount and recovery of carbon is given in Table V. This is evaluated both by extending burn times and by combusting with and without the catalyst. Carbon content appears to increase with decreasing particle size, although there are obvious sampling difficulties with the larger particle fractions 1 and 2. There is also a definite increment of carbon recovered with catalyst, suggesting the presence of amorphous or graphitic carbon, or both, and a plateauing of recovery (for fraction 5) at about 40 sec. An additional consideration involved completeness of carbon recovery of the larger particle fractions, particularly with the instrument limitation on combustion temperature. To test this, fractions 2, 3 and 4 of another aliquot of parent latite were normalized to the sample particle size of fraction 5 by porcelain mortaring. The results given in Table VI indicate substantially increased recovery after mortaring, but consistently lower carbon values in the originally larger particle size fractions. Again essentially quantitative recovery was observed for the 40 sec burns with some additional recovery in the presence of the oxidizing catalyst.

Two additional samples were analyzed in some detail—a Hawaiian basalt and a sample of the Pueblito de Allende meteorite. The latter sample was analyzed under standard burn conditions with and without catalyst. Complete computer analysis of duplicate and triplicate runs is given in Table VII. The reproducibility is very good and the values

for total N and C content are in reasonable agreement with data given previously by other techniques on samples from this meteorite. For example Cronin and Moore (6), using much higher combustion temperatures, give a value of 2500 for C and 60 for N.

Lastly a sample of Hawaiian basalt was similarly analyzed with and without catalyst and after porcelain mortaring. Values given without mortaring illustrate sampling and recovery problems, particularly when large particles are present. However after porcelain mortaring there is good reproducibility for all elemental components emphasizing the need for using samples of small particle size with this technique. Further the data for carbon are in agreement with 150 ppm reported by Kaplan et al. (7), using a different combustion technique, and 140 ppm reported by Burlingame et al. (8), using vacuum pyrolysis

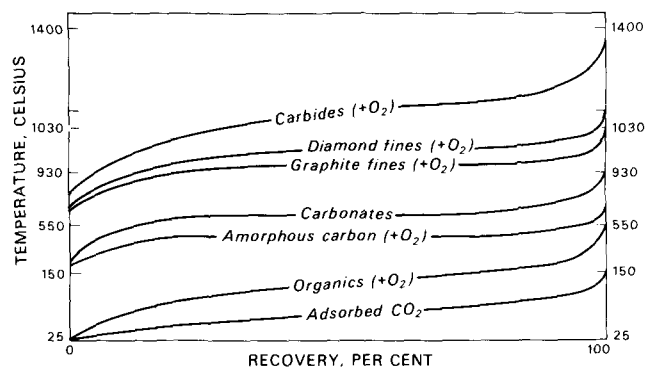


FIG. 9. Recovery of various forms of carbon using CHN elemental analysis and appropriate calcination.

TABLE VII
CHN Analysis of a Pueblito de Allende Meteorite Sample^a

24 Jul 70	Abundance, ppm			Atom ratios	
	N	C	H	N/C	H/C
No catalyst	39.4 (2.11)	1890.2 (100.9)	660.9 (35.28)	0.01789	4.17
	40.8 (2.67)	1882.8 (123.3)	657.1 (43.04)	0.01859	4.16
Plus catalyst	40.6 (2.79)	1887.3 (129.8)	660.4 (45.42)	0.01844	4.17
	38.4 (2.26)	1847.9 (108.9)	667.2 (39.30)	0.01781	4.30
	40.6 (2.57)	1855.5 (117.2)	655.2 (41.40)	0.01877	4.21

^aValues in parentheses are μg of N, C and H mass analyzed.

TABLE VIII
CHN Analysis of a Hawaiian Basalt, (I. Kaplan, BTS-17-50)^a

23 Jul 70	Abundance, ppm			Atom ratios	
	N	C	H	N/C	H/C
No catalyst	6.6 (0.40)	80.9 ^b (4.85)	38.9 (2.33)	0.0702	5.73
	8.8 (0.85)	119.8 (11.51)	52.1 (5.00)	0.0631	5.18
	11.9 (0.86)	117.5 (8.51)	49.2 (3.56)	0.0866	4.99
Plus catalyst	7.2 (0.34)	87.7 (4.21)	73.2 (3.51)	0.0702	9.95
	7.0 (0.36)	77.1 (4.01)	58.1 (3.02)	0.0773	8.99
29 Sep 70					
No catalyst	14.6 (1.03)	155.1 (10.86)	82.7 (5.79)	0.0810	6.35
Porcelain	12.2 (1.02)	144.7 (12.05)	78.7 (6.55)	0.0725	6.48
mortared	11.2 (0.57)	144.4 (7.33)	76.3 (3.87)	0.0662	6.30

^aSample range 51-96 mg. (Values in parentheses are μg of N, C and H mass analyzed.)

^bLarge glassy object included.

with analysis by high resolution mass spectrometry. Since Hawaiian basalt represents a good example of low level C, H and N analysis, it is worthwhile to present typical chromatograms used in this analysis. Figure 8 shows the chromatograms for an injection rod, rod + catalyst, the basalt and the low level daily CaCO_3 calibration, all at maximum sensitivity of the instrument.

Although application of this technique has been limited to several terrestrial samples and lunar material, reported elsewhere (9), some estimation of the forms of carbon present in a given sample may be made. This requires comparison of yields before and after appropriate step-wise calcination conditions. Thus calcination in the presence of oxygen at 150 C should remove adsorbed CO_2 and volatile organics. Additional calcination at 550 C should remove the remaining organics and amorphous carbon. Finally by extending burn times beyond the customary 20 sec time, an estimation of graphitics or diamond fines, or both, as well as the presence of refractory carbide may be made. Such analyses should be made with and without catalyst. The broad feature of an interpretive scheme are presented in Figure 9.

There are of course difficulties and limitations to this method. Among them are the unknowns involved in the chemical interactions of the various forms of carbon with compounds and elements present in the sample matrix. Further some noncontaminating procedure for reducing the particle size appropriately must be employed before analysis. However the method is sensitive, reproducible and gives a simultaneous analysis of C, H and N on each sample, allowing additional evaluation of sampling problems and random contamination. Also some improvements in stability, sensitivity and accuracy may be anticipated using a suitable electronic integrator to provide precise peak area measurements with either this stabilized column system or

with a standard instrument equipped with a Polypak (10) or Poropak Q column. Perhaps such analyses might have potential application in such diverse areas as the analysis of unusual geological specimens, petroleum engineering and possibly criminology.

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