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Comparison of Two Elemental-Analyzer Gas-Isotope-Ratio Mass Spectrometer Systems in the Simultaneous Measurement of $^{13}\text{C}/^{12}\text{C}$ Ratios and Carbon Content in Organic Samples

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Two commercial elemental-analyzer gas-isotope-ratio mass spectrometer systems (Finnigan Heraeus-Delta E and VG Carlo Erba-PRISM) were evaluated for their ability to analyze $^{13}\text{C}/^{12}\text{C}$ isotope ratios ($\delta_{\text{PDB}}^{13}\text{C}$, -30.71–1433.67‰) and carbon content (36–100%) in a variety of organic samples (isotope standards, chemical standards, agricultural products, and physiological fluids). On average, the VG system produced better agreements with the accepted values than did the Finnigan system. Significant memory effects were observed in the Finnigan system but were negligible in the VG instrument. The minimal sample size necessary to produce acceptable $\delta_{\text{PDB}}^{13}\text{C}$ values was 0.05 mg of C in the Finnigan system and 0.03 mg of C in the VG system. Liquid nitrogen consumption by the Finnigan instrument was 4 times greater than that by the VG system. In our hands, the VG system is superior to the Finnigan system for carbon isotope ratio and content measurements.

INTRODUCTION

The use of stable carbon isotopes in agricultural, clinical, and nutrition research generates large numbers of liquid and solid samples. These samples must be converted into CO_2 before the ^{13}C enrichment can be measured by gas-isotope-ratio mass spectrometry (GIRMS). The carbon content of these samples must be known to understand the efficiency of absorption, oxidation, and use of ^{13}C -labeled substrates. Carbon content can be measured during the manual combustion procedure using the manometric technique or separately using an elemental analyzer. The manual conversion of samples using the Dumas¹ or the sealed-tube combustion method² is tedious, labor intensive, and time consuming. Separate measurement of carbon content by an elemental analyzer requires larger amounts of the sample and additional steps in the procedure.

In 1985, Preston and Owens³ described an automated Dumas combustion system coupled to a GIRMS system for $^{13}\text{C}/^{12}\text{C}$ isotope ratio measurements. Subsequently, a Heraeus elemental analyzer interfaced to a Finnigan Delta-E GIRMS instrument and a Carlo Erba elemental analyzer interfaced to a VG PRISM GIRMS system became commercially available. However, the performance of these on-line combustion-GIRMS systems in measurements of carbon isotope ratio and carbon content in agricultural, clinical, and nutrition research has not been evaluated. Our objective was to evaluate the performance of these two commercially available instruments for $^{13}\text{C}/^{12}\text{C}$ isotope ratio and carbon content measurements made on a variety of materials with natural abundances and enriched levels of ^{13}C .

EXPERIMENTAL SECTION

Finnigan System. The Finnigan system (Figure 1A) consists of a Heraeus CHN-O-RAPID elemental analyzer (Heraeus, Hanau, Germany) and a Finnigan MAT Delta E GIRMS instrument

(Finnigan MAT, Bremen, Germany).

The elemental analyzer consists of an autosampler with a 55-sample carousel, a combustion tube containing cerium dioxide and copper oxide, and a reduction tube containing copper wires and lead chromate. All chemicals were supplied by Heraeus (Hanau, Germany). Samples are loaded in tin sample capsules (UIC Inc., Joliet, IL) and dropped sequentially from the carousel into the combustion tube under a helium gas stream (chromatographic grade; Big Three Industries, Houston, TX) flowing at 55 mL/min. Simultaneously, a pulse of oxygen (99.995%; Big Three Industries, Houston, TX) at 5 mL/min is admitted into the combustion tube causing flash oxidation (1700 °C) of the tin capsule and its contents. Complete oxidation of the sample is catalyzed by the cerium dioxide and copper oxide. Excess oxygen is removed and nitrogen oxide is converted to nitrogen gas by the copper wires in the reduction tube at 600 °C. Sulfur in the sample is removed by the lead chromate. Water produced from the combustion is removed by the first trap at -80 °C. Carbon dioxide is collected in the second trap at -180 °C. At the end of an 8-min cryogenic trapping, the helium carrier gas is diverted to the atmosphere whereas noncondensable gases remaining in the traps are pumped away. Subsequently, the water and CO_2 traps are isolated from the system and heated to 55 °C. After the CO_2 has expanded into the dual inlet of the mass spectrometer, the residual CO_2 and water vapor in the traps are pumped away.

The Finnigan Delta E is a dual-inlet triple collecting instrument with an electron impact source and an electromagnet. The filament current at 1–1.5 mA and electron energy at 80 eV were preset at the factory. The operation and data acquisition/analysis sequence is controlled automatically with a Compaq DeskPro 386 computer system (Compaq Computer Corp., Houston, TX). Each sequence takes approximately 24 min.

VG System. The VG system (Figure 1B) consists of a Carlo Erba NA 1500 nitrogen/carbon analyzer (Fisons Instruments, Dearborn, MI) and a VG PRISM GIRMS instrument (VG Isotech, Middlewich, Cheshire, U.K.).

The nitrogen/carbon analyzer has a 50-sample carousel, a combustion tube containing chromium trioxide and silvered cobaltous cobaltic oxide, and a reduction tube containing copper wires. All chemicals were ordered from Fisons Instruments (Dearborn, MI). Tin sample capsules are dropped sequentially from the carousel into the combustion tube with helium gas flowing at 80 mL/min. Simultaneously, a pulse of oxygen is introduced in the combustion chamber causing flash oxidation of the tin capsule and its content. The combustion products pass through the combustion tube, the reduction tube, a gas chromatography column, a water trap, and a CO_2 trap. Complete oxidation of the sample is catalyzed by the chromium trioxide and silvered cobaltous cobaltic oxide in the combustion tube. Halogenated and sulfurous gases produced during oxidation are removed by the silvered cobaltous cobaltic oxide. Excess oxygen is removed, and nitrogen oxides are converted to nitrogen gas by passage through the copper wires at 650 °C in the reduction tube. Carbon dioxide, nitrogen, and water are separated by gas chromatography on a Poropak QS column (4 mm i.d. \times 2 m) at 52 °C. Concentrations of these gases are measured by a thermal conductivity detector at 90 °C. Water vapor leaving the column is removed by the water trap at -80 °C. Carbon dioxide is condensed in the CO_2 trap at -180 °C. At the end of the cryogenic trapping (5 min), noncondensable gases remaining in the traps are pumped away. Trapped CO_2 is released by raising the temperature of the trap to 55 °C. CO_2 is allowed to expand into the

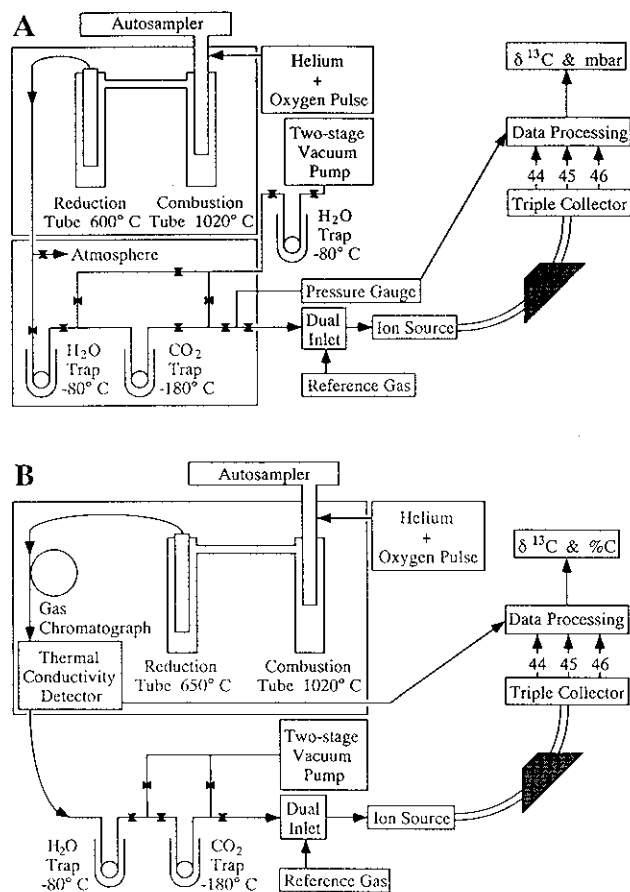


Figure 1. Schematic diagrams for (A) the Finnigan Heraeus-Delta E system and (B) the VG Carlo Erba-PRISM system.

VG PRISM GIRMS system for carbon isotope ratio measurements.

The PRISM is a dual-inlet triple-collecting instrument with an electron impact source and an electromagnet. For carbon isotope ratio measurement, we set the filament current at 220 μ A and the electron energy at 70 eV. The operation and data acquisition/analysis sequence is controlled automatically by an IBM PS/2 computer system (IBM United Kingdom Inc. Ltd., Greenock, Scotland). Each sequence takes approximately 20 min.

Carbon Isotope Ratio Measurements. Performance of the Finnigan Heraeus-Delta E and the VG Carlo Erba-PRISM systems for carbon isotope ratio measurements were evaluated using a variety of materials at natural abundances and enriched levels of ^{13}C . The $\delta_{\text{PDB}}^{13}\text{C}$ values obtained by each system were compared to the $\delta_{\text{PDB}}^{13}\text{C}$ values of the same samples obtained by the sealed-tube combustion method. Five aliquots of each sample were measured using the automated systems.

A tank of CO_2 (100% CO_2 , Big Three Industries, Houston, TX) was used as the working standard for both the Finnigan and the VG systems. The results are expressed in delta (δ), per mil (‰) units, as follows:

$$\delta^{13}\text{C}, \text{‰} = \left(\frac{R_{\text{sample}}}{R_{\text{ws}}} - 1 \right) \times 1000$$

where R_{sample} is the $^{13}\text{C}/^{12}\text{C}$ ratio of the sample and R_{ws} is the ratio of the working standard. For CO_2 generated from samples using the sealed-tube combustion method² the tank CO_2 was calibrated using two reference CO_2 gases (NBS-16 and NBS-18, National Bureau of Standards, Gaithersburg, MD). Before any manual or automated analyses, the tank CO_2 in each system was tested with a CO_2 gas prepared by manual combustion of a reference material, NBS-22. The parameters in the reference file were then adjusted to yield the theoretical $\delta^{13}\text{C}$ value of -29.6 ‰ for NBS-22. For the Finnigan Heraeus and the VG Carlo Erba systems, the tank CO_2 was further calibrated using NBS-22 prepared through the automated combustion systems. The $\delta^{13}\text{C}$ values measured against the tank CO_2 were converted to $\delta^{13}\text{C}$ values against PDB

($\delta_{\text{PDB}}^{13}\text{C}$) according to the procedures of Craig.⁴ The PDB is a Cretaceous belemnite from the Pee Dee Formation in South Carolina; it has a defined $\delta_{\text{PDB}}^{13}\text{C}$ value of 0 ‰.

Carbon Content Measurements. To determine their performance in carbon content measurements, each system was evaluated using isotopic and chemical standards of known carbon content (36.3–100%). Five aliquots of each sample were measured in the evaluation.

Carbon content was measured postanalysis in the Finnigan system from data on the pressure of the carbon dioxide generated after expansion of the gas into the fixed volume of the CO_2 trap (Figure 1A). The volume of the CO_2 trap was calibrated from pressure measurements of samples with known carbon content. The ideal gas law was used to calculate the volume of the trap. The quantity of CO_2 produced from each sample was calculated from the trap volume and the measured temperature and pressure. Software to perform these calculations is not available on the Finnigan system.

Carbon content was measured on-line in the VG system using the thermal conductivity detector readings (Figure 1B). The readings were calibrated daily using a chemical standard of known elemental composition at the beginning of each daily run.

Minimal Sample Size. Minimal sample size is defined as the smallest sample that would yield a $\delta_{\text{PDB}}^{13}\text{C}$ value within 0.5 ‰ of the accepted value with a repeatability of 0.5 ‰ or less. Cyclohexanone (2,4-dinitrophenyl)hydrazine (CDNPH) was used to determine the minimal sample size. CDNPH has a carbon content of 51.79% and a $\delta_{\text{PDB}}^{13}\text{C}$ value of -28.31 ± 0.04 ‰ ($n = 3$) by manual combustion. Amounts of CDNPH weighing approximately 0.01, 0.05, 0.1, 0.5, 1, 3, and 5 mg were prepared in replicate ($n = 5$) for each system using a Cahn C-31 microbalance (Cahn Instruments Inc., Cerritos, CA). The microbalance has a precision of 0.1 μg .

Memory Effect. Memory effects were determined by sequential combustion of 10 samples of NBS-22 ($\delta_{\text{PDB}}^{13}\text{C} = -29.63$ ‰), followed by 10 samples of ^{13}C -enriched rice cereal ($\delta_{\text{PDB}}^{13}\text{C} = 1213$ ‰), and again by 10 samples of NBS-22.

Manual Combustion. The accepted $\delta_{\text{PDB}}^{13}\text{C}$ values were obtained by conversion of all the samples to CO_2 , N_2 , and H_2O in triplicate using the sealed-tube combustion method.² Following cryogenic purification of the CO_2 , the $^{13}\text{C}/^{12}\text{C}$ isotope ratio of the CO_2 was measured against the tank CO_2 working standard using the VG PRISM GIRMS instrument.

Samples. Isotope Standards. NBS-21 (graphite) has an accepted $\delta_{\text{PDB}}^{13}\text{C}$ value of -28.10 ‰; NBS-22 (hydrocarbon oil) has a value of -29.61 ‰. Both standards were obtained from the National Bureau of Standards (Gaithersburg, MD).⁵ IAEA 309A and IAEA 309B, ^{13}C -enriched glucose standards obtained from the International Atomic Energy Agency (Vienna, Austria), have recommended $\delta_{\text{PDB}}^{13}\text{C}$ values of 93.9 and 535.3 ‰, respectively.⁶

Chemical Standards. Analytical-grade standards of acetanilide, atropine, CDNPH, and phenanthrene were obtained from Carlo Erba (Fisons Instrument, Dearborn, MI). D,L-Tryptophan was obtained from Merck & Co., Inc. (Rahway, NJ).

Labeled Agricultural Products. The ^{13}C -labeled agricultural materials were obtained from corn, rice, sorghum, soybeans, and wheat harvested from $^{13}\text{CO}_2$ -labeling studies. The kernels, grains, rice hulls, rice starch, and soybeans were separately milled using a Thomas-Wiley intermediate mill equipped with a 60-mesh screen (Arthur H. Thomas Co., Philadelphia, PA). The milled samples were further crushed with a mortar and pestle and then refrigerated until analysis.

Physiological Samples. Urine samples were collected from a human subject who had ingested lactose [^{13}C]ureide. The fresh urine samples were lyophilized and then refrigerated until analysis.

Statistics. A detailed pair-wise comparison⁷ for each sample type showing the mean difference (MD) and the limits of agreement ($\text{MD} \pm 2 \text{SD}$ of the differences) between the accepted $\delta_{\text{PDB}}^{13}\text{C}$ values and those measured using either the Finnigan or the VG system was made by plotting the differences (measured - accepted) against the means of the measured and the accepted $\delta_{\text{PDB}}^{13}\text{C}$ values. The same comparison was used to assess agreement between the theoretical carbon content and those measured by the two systems. Regression analysis was used to test for any significant relationship between the differences and the mean values.

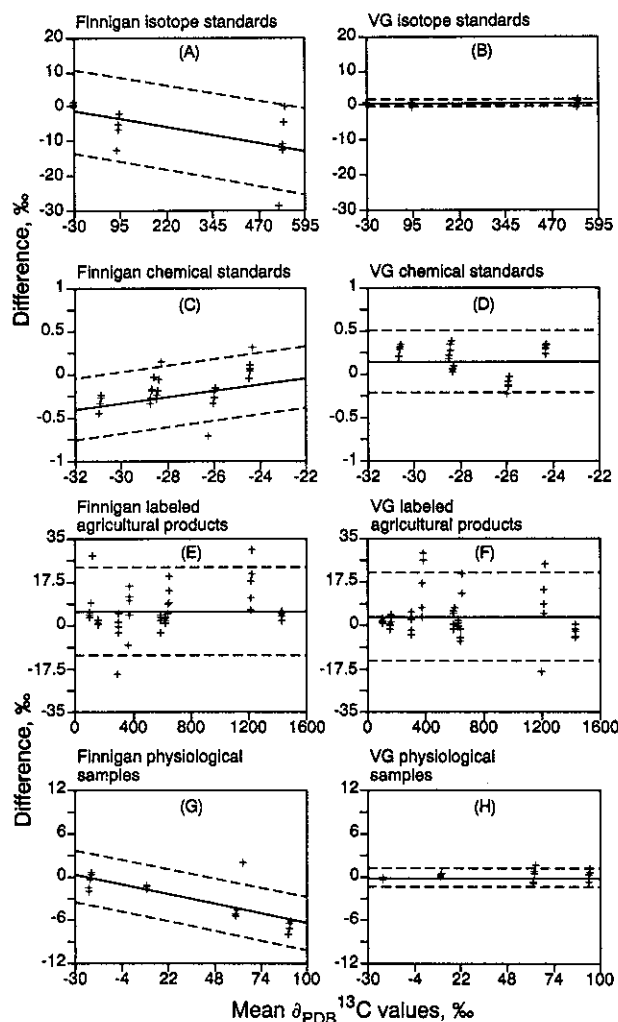


Figure 2. Bland and Altman's pairwise comparison between the accepted $\delta_{\text{PDB}}^{13}\text{C}$ values and those measured by the Finnigan Heraeus-Delta E system and by the VG Carlo Erba-PRISM system. In each comparison, the solid line represents the mean difference, the dashed lines represent the upper and lower limits of agreement, and the symbols (+) represent the individual differences.

RESULTS AND DISCUSSION

Carbon Isotope Ratio Measurements. Performance of the Finnigan Heraeus-Delta E and of the VG Carlo Erba-PRISM systems for carbon isotope ratio measurements are summarized in Table I and Figure 2. For isotope standards with $\delta_{\text{PDB}}^{13}\text{C}$ values between -27.77 and $+540.42$ ‰, the Finnigan system had a mean difference of -4.68 ± 7.35 ‰. Furthermore, the differences were significantly related ($p = 0.002$) to the mean $\delta_{\text{PDB}}^{13}\text{C}$ values (Figure 2A). For the same materials, the VG system had a mean difference of 0.08 ± 0.55 ‰ and limits of agreement between -1.01 and $+1.17$ ‰ (Figure 2B). No significant relationship was detected between the differences and the mean values in this comparison. For chemical standards with $\delta_{\text{PDB}}^{13}\text{C}$ values between -30.71 and -24.43 ‰, the Finnigan system had a mean difference of -0.19 ± 0.21 ‰ and a significant relationship between the differences and the mean $\delta_{\text{PDB}}^{13}\text{C}$ values (Figure 2C). A mean difference of 0.14 ± 0.18 ‰ and limits of agreement between -0.22 and $+0.50$ ‰ were obtained for the VG system (Figure 2D). For ^{13}C -labeled agricultural products with $\delta_{\text{PDB}}^{13}\text{C}$ values between 107.09 and 1433.67 ‰, similar agreements with the accepted values were observed for both the Finnigan (4.94 ± 8.64 ‰; Figure 2E) and the VG (2.86 ± 8.92 ‰; Figure 2F) systems. For physiological samples with $\delta_{\text{PDB}}^{13}\text{C}$ values between -20.99 and $+94.13$ ‰, a mean difference of -3.24 ± 2.93 ‰ was obtained using the Finnigan system (Figure 2G). Again the

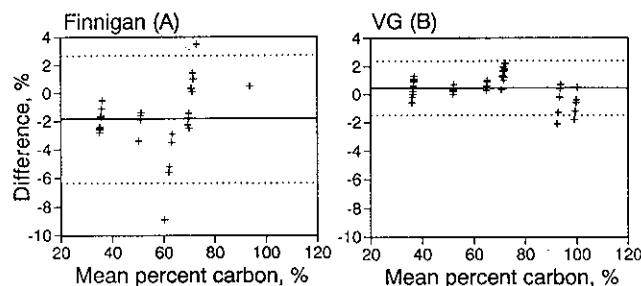


Figure 3. Bland and Altman's pairwise comparison between the theoretical carbon content and those measured by the Finnigan Heraeus-Delta E system (A) and by the VG Carlo Erba-PRISM system (B). In each comparison, the solid line represents the mean difference, the dashed lines represent the upper and lower limits of agreement, and the symbols (+) represent the individual differences.

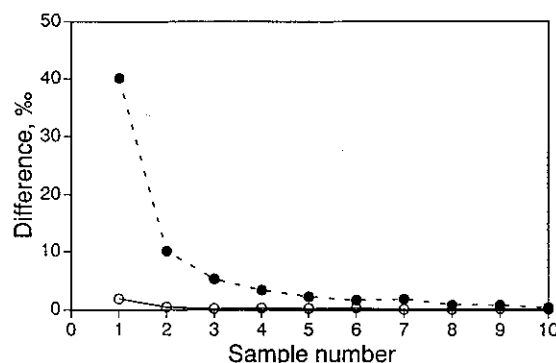


Figure 4. Memory effect for the Finnigan Heraeus-Delta E system (closed circles) and for the VG Carlo Erba-PRISM system (open circles). In both systems 10 samples of ^{13}C -enriched rice cereal were combusted; then 10 samples of NBS-22 were combusted.

differences were significantly related to the mean $\delta_{\text{PDB}}^{13}\text{C}$ values. With the VG system (Figure 2H), a mean difference of -0.07 ± 0.61 ‰ and limits of agreement between -1.31 and $+1.17$ ‰ were obtained.

Carbon Content Measurements. The performance of the Finnigan Heraeus-Delta E and the VG Carlo Erba-PRISM systems for carbon content measurements are summarized in Table II and Figure 3. For isotopic and chemical standards that had a carbon content between 36.3 and 100 ‰, the Finnigan system had a mean difference of -1.82 ± 2.26 ‰ and limits of agreement between -6.34 and $+2.70$ ‰ (Figure 3A). With the VG system, a mean difference of 0.46 ± 0.97 ‰ and limits of agreement between -1.48 and $+2.39$ ‰ were obtained (Figure 3B). Individual differences were not significantly related to the mean values in both comparisons.

Minimal Sample Size. The minimal sample size requirement for $^{13}\text{C}/^{12}\text{C}$ isotope ratio measurements was evaluated using CDNPH. The operating range for the Finnigan system was 0.1 – 5 mg of CDNPH, which corresponded to approximately 0.05 – 3 mg of carbon. The operating range for carbon isotope ratio measurements in the VG Carlo Erba-PRISM system was 0.05 – 5 mg of CDNPH, which corresponded to approximately 0.03 – 3 mg of carbon.

Memory Effect. Memory effects were significant in the Finnigan system but negligible in the VG system. After combustion of 10 samples of ^{13}C -labeled rice cereal with a $\delta_{\text{PDB}}^{13}\text{C}$ value of approximately 1215 ‰, the first NBS-22 sample gave a $\delta_{\text{PDB}}^{13}\text{C}$ value approximately 40 ‰ above the accepted value of -29.63 ‰. Nine successive samples of NBS-22 were required to bring the $\delta_{\text{PDB}}^{13}\text{C}$ value in the Finnigan system back to -29.63 ‰ (Figure 4). With the VG system, memory effect disappeared completely after two successive NBS-22 samples (Figure 4). The memory effect in the Finnigan system was not appreciably altered by in-

Table I. Agreement between the Accepted $\delta_{\text{PDB}}^{13}\text{C}$ Values Obtained by Manual Combustion and Those Measured by the Finnigan Heraeus-Delta E and the VG Carlo Erba-PRISM Systems

sample	accepted value (<i>n</i> = 3)	mean $\delta_{\text{PDB}}^{13}\text{C}$, ‰ (SD)			
		Finnigan		VG	
		(<i>n</i> = 5)	diff ^a	(<i>n</i> = 5)	diff ^a
Isotope Standards					
NBS-22 (hydrocarbon oil)	-29.63 (0.02)	-29.72 (0.37)	-0.09	-29.50 (0.16)	0.13
NBS-21 (graphite)	-27.77 (0.22)	-28.03 (0.23)	-0.26	-27.68 (0.13)	0.09
IAEA 309A (glucose)	95.53 (0.05)	89.05 (4.29)	-6.48	95.34 (0.50)	-0.19
IAEA 309B (glucose)	540.42 (0.20)	528.51 (10.85)	-11.91	540.71 (0.84)	0.29
mean diff (SD)			-4.69 (7.35)		0.08 (0.55)
Chemical Standards					
acetanilide	-30.71 (0.12)	-31.03 (0.09)	-0.32	-30.43 (0.05)	0.28
atropine	-28.55 (0.04)	-28.77 (0.12)	-0.22	-28.29 (0.08)	0.26
cyclohexanone	-28.31 (0.04)	-28.45 (0.17)	-0.14	-28.27 (0.02)	0.04
(2,4-dinitrophenyl)hydrazone					
tryptophan	-25.84 (0.14)	-26.20 (0.22)	-0.36	-25.98 (0.06)	-0.14
phenanthrene	-24.43 (0.13)	-24.35 (0.13)	0.08	-24.15 (0.04)	0.28
mean diff (SD)			-0.19 (0.21)		0.14 (0.18)
Labeled Agricultural Products					
soybeans	107.09 (1.52)	116.43 (10.32)	9.34	108.06 (0.66)	0.97
sorghum	159.54 (0.04)	160.08 (0.88)	0.54	159.72 (1.90)	0.18
rice cereal	303.22 (0.55)	299.17 (9.48)	-4.05	303.28 (3.33)	0.06
Lot 300					
rice hulls	374.73 (3.00)	380.95 (9.23)	6.22	390.54 (10.12)	15.81
wheat	596.04 (4.31)	596.07 (3.46)	0.03	598.71 (3.29)	2.67
wheat flour	627.51 (1.77)	629.25 (0.88)	1.74	627.18 (0.88)	-0.33
corn	644.87 (15.67)	655.45 (5.77)	10.58	646.25 (11.00)	1.38
rice cereal	1212.65 (6.45)	1229.18 (9.31)	16.53	1218.75 (14.31)	6.10
Lot 1200					
rice starch	1433.67 (1.22)	1437.16 (1.42)	3.49	1430.35 (1.91)	-3.32
mean diff (SD)			4.94 (8.64)		2.86 (8.92)
Physiological Samples					
urine 7-1	-20.99 (0.44)	-21.91 (1.17)	-0.92	-21.44 (0.12)	-0.45
urine 7-4	11.11 (0.16)	9.50 (0.23)	-1.61	11.16 (0.14)	0.05
urine 7-6	63.22 (0.85)	59.26 (3.15) ^b	-3.96	63.25 (0.91)	0.03
urine 7-10	94.13 (0.98)	86.86 (0.75) ^b	-7.27	94.22 (0.64)	0.09
mean diff (SD)			-3.24 (2.93)		-0.07 (0.62)

^a Difference = $\delta_{\text{PDB}}^{13}\text{C}$ measured by automated analysis - $\delta_{\text{PDB}}^{13}\text{C}$ measured manually. ^b *n* = 4.

^a Difference = $\delta_{\text{PDB}}^{13}\text{C}$ measured by automated analysis - $\delta_{\text{PDB}}^{13}\text{C}$ measured manually. ^b *n* = 4.

Table II. Agreement in Carbon Content Measurements between the Theoretical Values and Those Measured Using the Finnigan Heraeus-Delta E and the VG Carlo Erba-PRISM Systems

sample	theor	mean % C (SD)			
		Finnigan		VG	
		(<i>n</i> = 5)	diff ^a	(<i>n</i> = 5)	diff ^a
IAEA 309A (glucose)	36.3	34.8 (0.8)	-1.5	36.3 (0.3)	0
IAEA 309B (glucose)	36.3	34.0 (0.4)	-2.3	37.3 (0.2)	1.0
cyclohexanone (2,4-dinitrophenyl)hydrazine	51.79	49.7 (0.8)	-2.1	52.1 (0.2)	0.3
tryptophan	64.70	59.5 (2.3)	-5.2	65.4 (0.2)	0.7
atropine	70.56	69.8 (1.6)	-0.8	71.9 (0.5)	1.3
acetanilide	71.06	71.5 (2.1)	0.4	72.7 (0.4)	1.6
phenanthrene	93.39	93.9 ^b	0.5	92.9 (1.1)	-0.5
NBS-21 (graphite)	100	130.6 (22.0)	30.6	99.3 (0.8)	-0.7
mean diff (SD)			-1.6 (2.0) ^c		0.5 (0.8)

^a Difference = % C measured by automated analysis - theoretical % C. ^b The weights of four of the five samples were beyond the operating range of the instrument. ^c NBS-21 data were excluded from mean difference calculations.

creasing the time between successive samples from 30 s to 5 min.

Liquid Nitrogen Consumption. The Finnigan system consumed liquid nitrogen at an average rate of 4 L/sample. This consumption rate is approximately 4 times higher than that of the VG unit.

CONCLUSION

In three out of four comparisons, carbon isotope ratio measurements (Figure 2) from the VG Carlo Erba-PRISM

system agreed better with the accepted $\delta_{\text{PDB}}^{13}\text{C}$ values than did the measurements from the Finnigan Heraeus-Delta E System. No significant relationships were observed between the individual differences and the mean $\delta_{\text{PDB}}^{13}\text{C}$ values from the VG system in any of these comparisons. Significant relationships were detected, however, between the individual differences and the mean $\delta_{\text{PDB}}^{13}\text{C}$ values from the Finnigan system in three of the four comparisons. Carbon content measurements (Figure 3) from the VG system also agreed better with the theoretical carbon contents than did the

measurements from the Finnigan system. Furthermore, the Finnigan system has two substantial problems: the significant memory effect (Figure 4) and the inability to measure carbon content on-line. In our hands, therefore, the VG system is superior to the Finnigan system for both carbon isotope ratio and carbon content measurements.

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