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INORGANIC ANALYSIS IN A CONTROLLED ECOLOGICAL LIFE SUPPORT SYSTEM

FINAL REPORT ON NASA GRANT NAG2-170
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INORGANIC ANALYSIS IN A CONTROLLED ECOLOGICAL LIFE SUPPORT SYSTEM

FINAL REPORT

INTRODUCTION

This program has investigated techniques useful for the elemental analysis of samples of types which might require analysis within a controlled ecological life support system (CELSS). Such analyses might be required in an operational CELSS to monitor elemental cycles, to assure the safety and nutritional adequacy of recycled products such as potable water and food or to investigate unanticipated control or materials problems.

Two aspects of the elemental analysis problem were chosen for study. The first dealt with the resources required to carry out such analyses. The purpose of this inquiry was to assist planners, not intimately familiar with elemental analysis, better appreciate the potential problems associated with the integration of current analytical technology into a CELSS design. The desired information was obtained by carrying out elemental analyses on CELSS relevant samples. The second area of inquiry dealt with the problem of obtaining chemical information in addition to elemental composition. As in some environmental, nutritional and corrosion studies, information about the chemical bonding or oxidation state of an element may be of importance in a CELSS. The additional information can be obtained by separating the components of the sample and analyzing each component. Chromatographic techniques that can provide the necessary separations are available, but interfacing the chromatograph with an elemental analyzer is still an area of active research. The second part of the study emphasized the investigation of potential interfacing techniques.

The technique for elemental analysis utilized in this study was inductively coupled plasma optical emission spectrometry (ICPOES). This technique was chosen because it can provide both qualitative and quantitative information for virtually all elements of interest in a CELSS. In addition the technique is rapid and amenable to a high degree of automation. The ICPOES instrumentation referred to in this report is a Perkin-Elmer Corp. Model ICP 5000 upgraded to Model ICP 5500 capability.

The ICPOES technique is a nearly universal elemental detector because of the high degree of electronic excitation which occurs as the sample material moves through the very hot plasma. Relaxation to the ground electronic state results in the emission of photons with energies characteristic of the elements making up the sample. Observation of the emission intensity versus wavelength provides both qualitative and quantitative information about the elemental composition of the sample.

Current generation ICPOES systems require that the sample be in the liquid state for analysis. The sample liquid is nebulized to form an aerosol which after removal of the larger droplets is conducted up into the plasma torch. Water quality analysis and other low concentration homogeneous phase liquid samples generally do not require any sample preparation. Solid samples must, however, be taken into solution, a process commonly referred to as ashing or digestion.

This report provides an overall summary of the work carried out during the program. More detailed accounts of some aspects of this study will be published in scientific journals or the theses of students who have participated. Dr. David Smith has described his contribution to the interfacing study in his Ph.D. dissertation, "Fundamental Studies of Aerosol Sample Introduction in Optical Atomic Spectrometry", presented to the Graduate Division of the Georgia Institute of Technology in September 1983.

RESOURCES REQUIRED FOR THE ANALYSIS OF CELSS SAMPLES

A description of the preparation and analysis of a batch of freeze dried feces for use by CELSS researchers is provided in Appendix 1. This section deals with the resources required to carry out this procedure. It is assumed that a sufficiently large sample is taken to be representative and that the sample is homogenized so that a conveniently small aliquot can be taken for digestion and analysis.

It is useful to divide the resource requirements into those associated with sample preparation and those associated with sample analysis.

1. Sample Preparation

An acceptable procedure (based on that used at the US Department of Agriculture's Human Nutritional Research Laboratory at Grand Forks, North Dakota) for the preparation of fecal material for ICPOES analysis involves the freeze drying of the fecal material to establish a reproducible water content, grinding the residue in a dry atmosphere to produce a homogeneous sample, digestion of an aliquot of sample using a wet oxidative process, making the sample solution to volume and proceeding with the analysis.

A number of digestion procedures have been evaluated on fecal solids. We have investigated dry ashing in a muffle furnace, mixed acid digestion utilizing sulfuric and nitric acids, nitric acid and hydrogen peroxide oxidation, and high pressure nitric acid digestion in a sealed container (Parr Bomb). The later procedure produced the most accurate results when

evaluated using NBS Standard Reference Materials, thus it will be used in this example.

Table 1 contains a list of the materials and equipment required for this procedure. Both the weight and power consumption associated with each item have been proportioned over the number of samples which the item can process at the same time. For example the oven for heating the digestion bombs has a capacity of 20, thus its total power consumption of 3700 watt hr during a digestion procedure gives a power consumption of 180 watt hr per sample. Some items like the analytical balance and sample grinder can only be used on one sample at a time. The deionized water estimate includes the weight of resin and associated plumbing proportioned over the total volume of acceptable quality water derivable from the resin. The other reagents listed include the weights of associated dispensers and storage containers.

Both the mass of equipment and power required are surprisely large. If digestion of the sample was unnecessary, that is, if the solid or a slurry of the solid could be analyzed directly, a 35% reduction in the mass and 49% reduction in the power could be realized. This assumes freeze drying is still necessary to obtain a reproducible water content and that homogenization is required.

Table 2 lists the significant operations associated with sample preparation and gives an estimate of the time required for each. The first column gives the total time required for an operation. For example, approximately 12 hr are required to freeze dry the fecal material, although multiple samples can be dried at the same time. Single sample operations such as grinding and mixing are indicated with an asterisk and the times given are on a per sample basis. The column labeled "operator time/sample" indicates the actual technician time required to prepare and/or carry out the operation on a single sample.

Based on the results in the first column, approximately 22.5 hr are required to prepare a batch of 10 samples. This task would require 6.2 hr of technician time. Eliminating the sample digestion would reduce the total time by 29% and the technician time by 32%.

2. Instrumental Analysis

With the sample in solution the instrumental determination of elemental composition by ICPOES can begin. This process involves a calibration of the wavelength seeking routine of the monochromator, and emission intensity versus elemental concentration for each line to be used (generally one per element), and a background emission intensity for each line. During the analysis the monochromator rapidly slews to a wavelength near that of one of the analytical lines, slowly scans across the line measuring the emission intensity at each step and repeats the procedure for the remainder of the

Material/Equipment Item	Weight (kg)	Power (watt hr)
Freeze drier	7	115
Sample grinder	1	82
Parr bomb	1	--
Analytical balance	7.7	--
Local exhaust for bomb opening	5	10
Oven to heat bomb	3.5	180
25 ml volumetric flask	0.03	--
deionized water	0.1	--
Fuming nitric acid	0.01	--
Concentrated nitric acid	0.05	--
Total per sample	24.0	387

Table 1. The per sample weight and power consumption associated with the items required for sample preparation.

Operation	Total Time (min)	Operator Time (min/sample)
Freeze drying	720	2
Grinding and mixing	15*	15
Weighing	5*	5
Sample into Parr bomb	1*	1
Atmospheric pressure digestion	60	1
Bomb sealing	3*	3
Sealed bomb digestion	240	1
Bomb cooling	60	1
Bomb opening	5*	5
Digestate to volumetric flask	2*	2
Dilution to volume	1*	1
*Time required for each sample		
Total analyst time per sample		37

Table 2. The total time period required for completion of an analytical step, and the length of time a technician must spend on the step on a per sample basis.

Item	Power/Sample (watt hr)	Volume (cubic meter)
Monochromator	2.5	0.35
Torch	--	0.09
RF Power Supply	48	0.57
Data System	1.7	0.10
Printer	--	0.04
Totals	52.2	1.15

Table 3. Utilities required to analyze one sample for one element using our ICPOES system and the volumes of the instrumentation.

lines. Normally each line is analyzed three to five times to overcome the noise in the analytical system. The instrument microprocessor takes the set of intensities for each line, calculates the mean and dispersion for that line then using the concentration calibration for that line, calculates the corresponding elemental concentration in the sample. In our experience approximately one minute of analysis time is required per element per sample including the time involved in the calibration procedure.

Operation of our ICPOES requires a number of utilities. These include electrical power (see Table 3), 0.5 liters per minute of water to cool the plasma rf coil, 10,000 liters per minute of exhaust to remove excess heat from the rf generator and plasma fumes and 15 liters per minute of argon to operate the plasma torch.

Table 3 gives the electrical power consumed during required to carry out an analysis of a single sample for a single element using our ICPOES system. The volumes of the components are also given. The total mass of the instrumentation is approximately 200 kg.

INTERFACING A CHROMATOGRAPH AND ICPOES DETECTOR

The interface between a liquid chromatograph and a plasma emission source is currently the weakest link in the system. Typically, such interfaces are, at best, 2% efficient and often the efficiency is poorer. This results in quite inadequate sensitivity for the complete elemental analysis system. The thrust of the present research effort is to improve the efficiency of this interface, in order to make the use of a coupled ion chromatography/inductively coupled plasma (ICP) system an effective ion monitoring device. Our evaluation of this interface included a consideration of the effects of a low-g environment.

1. Direct Injection Device for IC/ICP Interfacing

The simplest approach to coupling an ion chromatograph with an ICP is to generate a fine liquid jet, with adequate velocity to penetrate the thermal barrier presented by the plasma, and pass it directly into the plasma. Such an approach was attempted in this study. A 10 um diameter liquid jet was produced by pumping liquid with a high performance liquid chromatography pump, and coupling the jet to a specially modified plasma torch assembly. The jet was able to penetrate the plasma readily, but the solvent evaporation and particle vaporization rates were relatively slow. Consequently, little atomization and excitation took place in the few milliseconds of exposure available in the plasma. Emission signals could be detected, but were only

weak and intermittent.

2. Hydraulic Jet Bead Impaction Device

As the plasma was clearly not able to vaporize a liquid jet directly, various approaches to the production of fine aerosol droplets with a small mean diameter and narrow size range were attempted. One approach used was to impact a high velocity liquid jet onto a spherical glass surface. The jet shatters on impact into an aerosol of small mean particle size. Unfortunately, a substantial mass of the sample is lost by sticking to the surface of the bead, making the process less efficient than is desirable.

3. Development of Monodisperse Aerosol Generator (MAG1)

The monodisperse generator originally envisioned for these studies, the Berglund-Liu generator, proved to be difficult to operate in the particle size range needed for direct ICP injection (e.g. 10-20 um). This was due primarily to design limitations inherent in the system, but also to limitations in the principle on which the device operated. As a consequence of these problems, we have developed a monodisperse aerosol generator of our own design (MAG1), which we believe to be greatly superior to, and much simpler to operate than the Berglund-Liu design.

The new design monodisperse aerosol generator operates on the principle of Rayleigh breakup in a liquid jet, followed by rapid gaseous dispersion of the droplets produced, in order to prevent coagulation. A schematic of the device is shown in Figure 1. The generator body is machined from 316 grade stainless steel and the nebulizer tips are fabricated from glass. These are made by collapsing fine bore capillary tubing until sealed, and then sanding the tips open again with fine grade silicon carbide paper. Perfectly circular openings in the range 3-50 um can readily be prepared by this means. Because of the likelihood of particulate blockage occuring, the entire device is thoroughly cleaned by ultrasonic means before assembly, and 0.2 um pore size filters are inserted in the liquid line at the solvent reservoir and in the generator just prior to the capillary tip.

The nebulizer can be operated over a wide range of gas and liquid flows, but for the present studies a liquid flow of 0.5 mL/min and a gas flow of 1.0 L/min proved to be convenient. The liquid stream is pumped at approximately 300 psi by a dual reciprocating pump, and issues from the capillary as a high velocity jet. The jet spontaneously breaks up into uniform droplets within a fre mm of the tip, but these rapidly coagulate to form larger droplets unless a gas jet is used to disperse them. The dispersing gas is in the form of a

high velocity jet, positioned accurately with relation to the liquid jet by means of an X-Y precision adjustment.

The effectiveness of the new nebulizer was determined by measuring the particle size distribution produced by the device, using laser Fraunhofer scattering equipment. The distribution (compared to a conventional pneumatic nebulizer) is shown in Figure 2 for a 10 um orifice. Essentially all the aerosol droplets are in one size range of the particle sizing device, which indicates a high degree of monodispersity. The particle size of the aerosol produced by the nebulizer can be readily estimated, without the need for particle size measurements, by applying Rayleigh's treatment. According to theory, the particle diameter should be approximately 1.89x the liquid jet diameter. This was confirmed experimentally, within +10%.

The analytical performance of the MAGI nebulizer was tested, on a preliminary basis, by generating an aerosol of approximately 20 um droplets, containing 10 ppm Mn in aqueous solution, and passing this through tygon tubing into an Ar ICP. The result of the tests was that the plasma was extinguished by the aerosol stream in every instance. While this might appear to be a severe setback, in fact it is very encouraging, because it indicates a sufficiently high water loading in the plasma to cause its extinction, which in turn implies a very high transport efficiency for the system. Clearly, what is called for is desolvation of the aerosol stream prior to introduction to the plasma. Studies incorporating desolvation of the aerosol are currently underway.

4. Implications of Present Studies in Low-g Environment

The studies described in previous sections of this report show considerable potential for monodisperse aerosol generation applied to ion chromatography/inductively coupled plasma interfacing. However, it is also clear that there are liable to be certain problems for the generation and transport of aerosols in a low-g environment. For example, gravitational settling is a major sizing process when using the hydraulic jet impaction bead device. This device also depends on gravity to remove sample solution that collects on the impaction bead. In the case of the MAGI design, the stability of the aerosol after eration by the air jet may be very different in low-g. The uncertainties associated with the behavior in low-g of polydispersed or monodispersed liquid aerosols suggest that an ideal for such an environment would allow the production of a solvent-free, highly dispersed aerosol with very small particle size.

The most effective means of generation for solvent-free aerosol is probably an electrothermally heated furnace similar to those used in atomic absorption spectrometry. Such devices are the object of fundamental studies by a few groups in the USA and the UK.

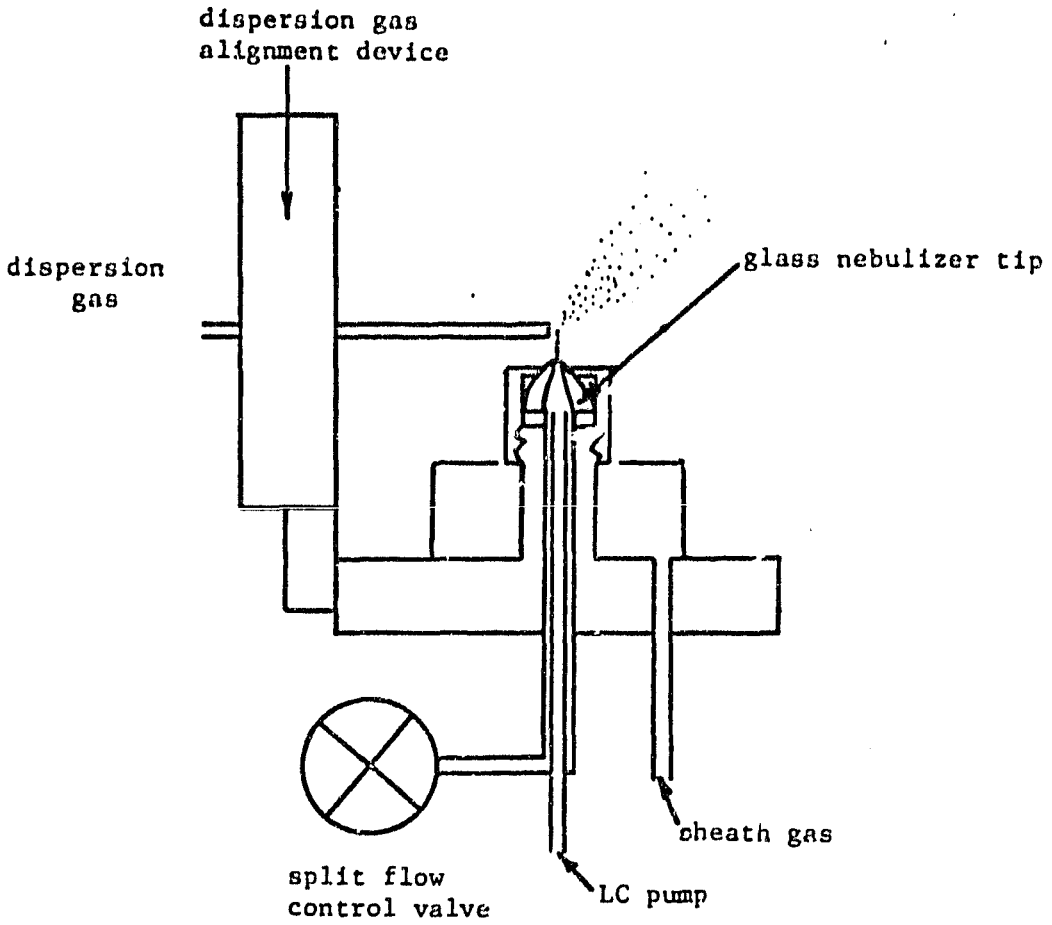

Figure 1. Monodisperse Aerosol Generator (MAG1)

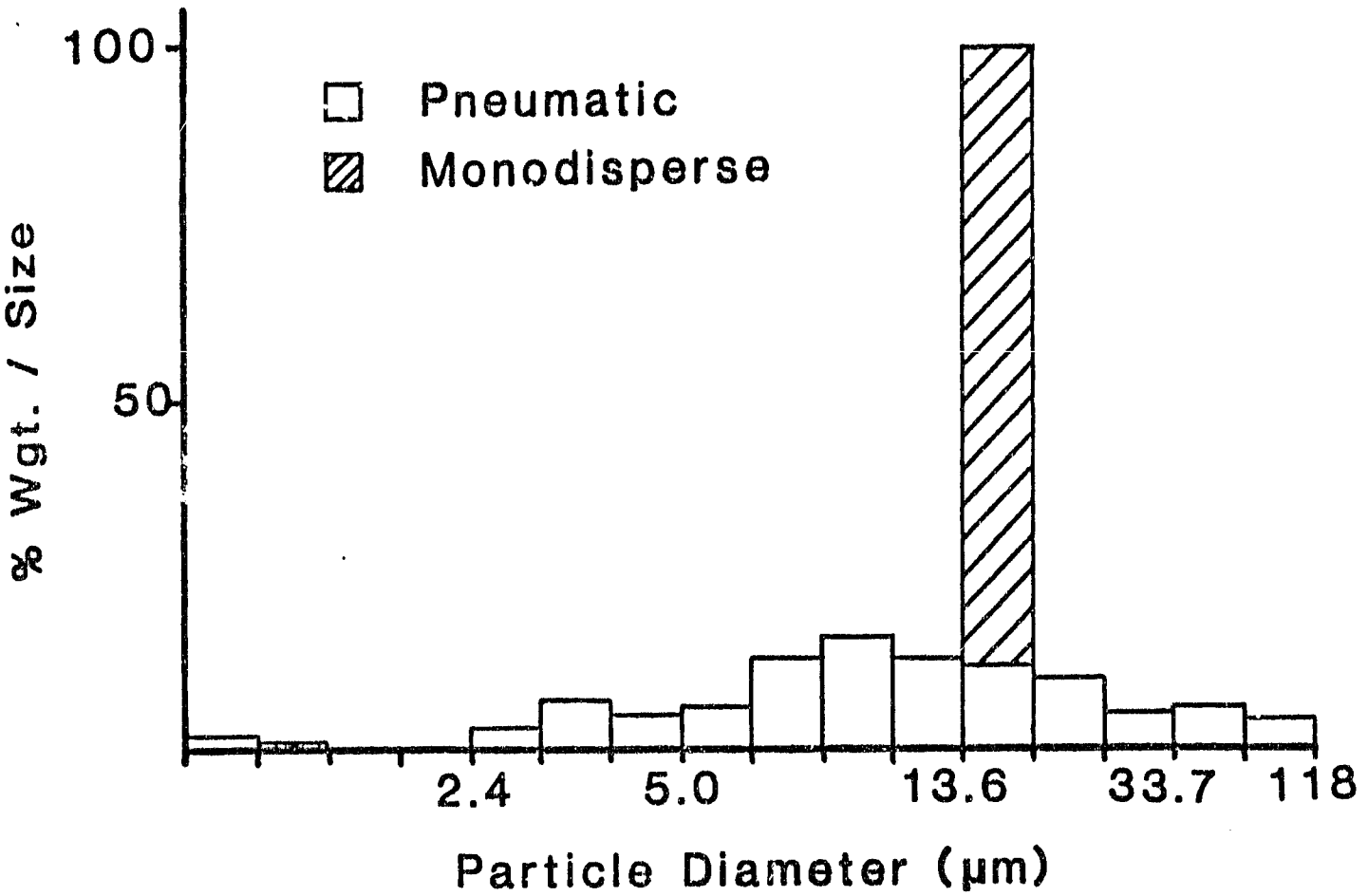

Figure 2. Droplet Distribution for Pneumatic and Monodisperse Aerosol Generation. Measurements of Fraunhofer diffraction from aerosols generated from a Perkin-Elmer crossed flow pneumatic nebulizer and the monodisperse aerosol generator designed for the LC/MS interface (6 µm orifice).

APPENDIX 1

NASA CELSS

Standard Research Materials

Freeze Dried Human Feces and Urine

Preparation and Analysis of Batch 2

by

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STANDARD RESEARCH MATERIALS: FECES AND URINE

Introduction

The importance of reliable standard reference materials to the assurance of comparability of results has long been recognized and the need filled largely by the National Bureau of Standards Office of Standard Reference Materials. Similar materials, including human feces, human urine, food preparation waste, and serafil, have been prepared for the NASA CELSS Program.[1] Demand for the fecal and urine materials has diminished the supply so that additional stocks are required. This report describes the preparation and analysis of Batch 2 of the human feces and urine Standard Research Materials.

Preparation of the Standard Research Materials

Freeze dried samples of human feces and urine (approximated, 1 Kg combined) were obtained from the U.S. Department of Agriculture Human Nutritional Research Laboratory in Grand Forks, North Dakota. These materials were transferred (in a dry nitrogen purged glove box) into 2 large plastic bags and homogenized. Aliquotes of each were then placed in an air tight blender jar, removed from the glove box, decontaminated and ground using a Sears Roebuck & Co. Model 400.E29604 blender. This combination of small blender and sealed jar allowed the system to be inverted and precessed producing a fine uniform powder. The sealed containers were then returned to the glove box, the materials recombined, mixed and loaded into 19 pre weighed 250 ml plastic bottles with tightly sealing caps. The bottles were removed from the glove box, decontaminated with 10% sodium hypochloride solution and labeled.

Preparation of Samples for Analysis

Analyses for Mg, Ca, Si, Na, K, Zn, Cu, Mn, S, B, Fe, V, P, Cr, and Ni were attempted using a Perkin-Elmer ICP Model 5500 inductively coupled plasma optical emission spectrometer. Samples, each taken from a different bottle, were prepared for analysis in one of three ways. One gram nominal samples of feces and NBS 1571, "orchard leaves", were weighted into crucibles, wetted with saturated $Ba(OH)_2$, heated slowly in a muffle furnace to 150°C to dry and then to 600°C and held for 10 hours to ash the carbonaceous matrix. One hundred mg samples of feces and NBS 1571 were weighed into Teflon lined Parr Acid Digestion Bombs, mixed with 2.75 ml of 10% fuming nitric acid in concentrated nitric acid, sealed and held at 120°C for 4 hours. One gram and 100 mg samples of urine were mixed with 2.75 ml of the above acid solution and allowed to react completely. Samples prepared by the first two methods were made to 25.0 ml and those by the third to 50.0 ml

Elemental Analysis

The spectrometer was calibrated using two standards for each element over the concentration range of interest and the "standard instrumental conditions", provided by the instrument manufacturer, were used for the analyses. The computer automated features of the instrument were fully utilized. Table 1 shows the results of the analysis of NBS 1571 prepared by the first method and table 2 the results when prepared by the second method. Clearly the accuracy for most elements is unacceptable.

A second set of samples was prepared using the second and third methods and analysis was performed by manually operating the ICP system. Table 3 shows the results of the analysis of NBS 1571. The errors indicated are reasonable for the combined uncertainties associated with the sample digestion, instrument calibration, and analytical methodology used.

Composition of Standard Research Materials:

Feces, Batch 2 and Urine, Batch 2

Table 4 gives the observed compositions of these two materials. The concentrations reported for Ca, Mg, Zn, Fe, P, Na, and K were obtained from samples prepared using the second and third methods followed by manually controlled ICP analysis. Three samples of each type were prepared and each sample analysis (based on a 5 second integrated emission intensity determination) was repeated 5 times for a total of 15 measurements for each element for each material. The number in parentheses following the elemental concentration is the total range i.e., the difference between the largest and smallest concentration observed. The absolute accuracy of the concentrations reported for these elements, with the possible exception of Na, should be better than ±20%. Sodium is less certain because NBS 1571 has a Na concentration which is too low to adequately evaluate the procedure. The valves for B, Mn, Cr and Cu are based on the analyses of from 3 to 6 samples per element. These analyses were carried out along with those reported in Tables 1 and 2. Based on the NBS 1571 results and results for other elements the values reported are probably 10 to 15 percent low. The absolute accuracy of the values for B and Mn, excluding this -10 to -15 percent systematic error should be better than ±20%. The values for Cr and Cu should be considered estimates. The values obtained for Cu in 5 fecal samples were very consistent (7% RSD), but the poor accuracy observed on NBS 1571 places their accuracy in doubt. Ni and V were not detected.

The values reported for C, H and N were obtained using a Perkin-Elmer Model 240 B Automatic CHN Analyzer. The value reported for S was obtained using the Schoniger Combustion Technique followed by titration with BaCl using Thorin indicator. Two samples of each material were analyzed.

An attempt was made to analayze for S using the ICP. The analytically useful S lines are in the vacuum UV making it necessary to purge the spectrometer optics with a gas free of O_2. When this was attempted it was found that the optical density of the light path varied resulting in a drifting emission signal. Inspection indicated that the monochromator housing and transfer options had not been properly resealed when the instrument was upgraded by Perkin-Elmer last year from a Model 5000 to a model 5500.

Discussion of the Methodology

The improved accuracy of the results reported in Table 3 over those in Tables 1 and 2 is believed due to improved solution matrix matching. The samples associated with Tables 1 & 2 were digested by the techniques indicated and then made to volume using 5% nitric acid. The standards were then prepared by diluting with the same 5% nitric acid solution. The results reported in Table 3 as well as most of those in Table 4 were obtained from samples digested in 2.75 ml of fuming nitric/nitric acid mixture. The standards were prepared by adding 2.75 ml of the same acid mixture. All of these solutions were diluted to volume with distilled water.

Prior to analysis the samples were dried in a convection oven held at $85^{\circ} \pm 1^{\circ}$ for 10 hours. The average weight loss during drying was 3.1% for urine and 4.4% for feces.

The digestion methods used in this study leave a small quantity of solid residue with NBS 1571 and feces. In the case of NBS 1571 this material is siliceous in nature. The same may be true for feces. The presence of a precipitate can lead to the loss of elements of interest by their participating as a bulk constituent of the solid, coprecipitation or adsorption. Dissolution of all solids is desirable but the presence of glass and quartz in the ICP torch assembly prevents the use of HF, the only feasible reagent for dissolving the precipate.

REFERENCES

1. Carden, J. L., and Browner, R. F., Preparation and Analysis of Standardized Waste Samples for Controlled Ecological Life Support Systems, NASA Contractor Report 166392, August 1982.

Element	Measured µg/g	Certified	Percent Error
Na	772	82±6	+840
Zn	29	25+3	+ 16
Cu	1.4	12±1	- 88
Mn	83	91±4	- 9
B	29	33±3	- 12
Fe	250	270	- 7
V	0.5		
P	1300	2,100±100	- 38
Ni	1	1.3±0.2	- ?

Table 1. Compositon of NBS 1571, "orchard leaves", following dry-ashing and computer controlled ICP analysis.

Element	Measured µg/g	Certified	Percent Error
Mg	4,900	6,200±200	-21
Ca	18,300	20,900±300	-12
Na	101	82±6	-23
K	8,050	14,700±300	-45
Zn	17	25±3	-32
Cu	3	12±1	-75
Mn	78	91±4	-14
B	29	33±3	-12
Fe	183	270	-32
P	1,300	2,100±100	-38
Ni	5	1.3±.2	250

Table 2. Composition of NBS 1571, "orchard leaves", following high pressure acid digestion followed by computer controlled ICP analysis.

Element	Measured µg/g	Certified µg/g	Percent Error
Ca	21,800±350	20,900±300	4
Mg	6,700	6,200±200	8
Zn	26.5±0.5	25±3	6
Fe	240±8	270	-11
P	1,930±30	2,100±100	-8
K	13,000±50	14,700±300	-12

Table 3. Composition of NBS 1571, "orchard leaves", following high pressure acid digestion and manually controlled ICP analysis.