On line and *in situ* quantification of gas mixtures by matrix interval algebra assisted quadrupole mass spectrometry

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A novel, efficient technique to identify and quantify complex gas mixtures is described. This approach can be applied on line and *in situ* and is extendible to samples with reactive and thermally labile species. Complex hydrocarbon mixtures are prepared in test experiments by irradiating frozen methane targets with 9 MeV α particles in an ultrahigh vacuum chamber and releasing them during successive heating of the solid samples from 10 to 293 K after each ion bombardment. A quadrupole mass spectrometer monitors time-dependent ion currents of selected m/z values, which are proportional to partial pressures in the case of a nonoverlapping fragmentation pattern. Predominantly, parent molecules and fragments of different molecular species add to a specific m/z value, i.e., $C_2H_4^+$, N_2^+, and CO^+ contribute to $m/z=28$. Programmed m/z ratios are chosen to result in an inhomogeneous system of linear equations including the measured ion current (right-hand vector), partial pressures (unknown quantity), and the calibration factors of fragments of individual gases determined in separate experiments. Since all quantities are provided with experimental errors, matrix interval algebra, i.e., an IBM high accuracy arithmetic subroutine defining experimental uncertainties as intervals, is incorporated in the computations to extract individual, calibrated components of complex gas mixtures. This proceeding enables the quantitative sampling of calibrated hydrocarbons, and, especially, H_2 and D_2 without further time-consuming preseparation devices on line and *in situ*, hence justifying the use of this approach in space missions to elucidate the chemical composition of, e.g., planetary atmospheres without payload wasting gas chromatographs. © *1995 American Institute of Physics.*

I. INTRODUCTION

Information on the chemical composition of planetary atmospheres is obtained *ex situ* by spectroscopic remote sensing in emission, reflection, or absorption in the microwave up to the ultraviolet region of the electromagnetic spectrum.[1] In the case of optically thick atmospheres, e.g., the Saturnian satellite Titan, however, these techniques can only supply data of outer atmospheric regions, and an *in situ* exploration of the low-altitude atmosphere down to the surface is required. The payload of the Huygens probe, i.e., part of the NASA/ESA Cassini space mission to Titan,[2] for example, comprises a gas-chromatograph-mass spectrometer (GCMS) device to explore Titan's atmospheric profile.

In terrestrial-based laboratories, GCMS serves as a powerful tool for quantitative analyses of complex gas mixtures.[3] Optionally, minor gas components are preconcentrated before their GC separation, e.g., trapping hydrocarbons at 77 K in a Tenax-GC tube and releasing the gases by a heat gradient desorption process.[4] Adapting GCMS to planetary missions, however, suffers from three fundamental restrictions. These off line and *ex situ* techniques exclude identification of thermally labile species, e.g., cyclobutadiene, C_4H_4, or reactive radicals such as CH, CH_2, and CH_3 which decompose in the GC capillary or react with the coating material. Reactive intermediates, however, play an important role in the photochemistry of outer planets of our solar system.[1] Further on, GCMS requires time-wasting preseparation techniques. Finally, prospective space missions to comets (the ROSETTA-project) or Pluto center on payload-saving analytical devices to probe atmospheres: the elimination of gas chromatographs gains considerable payload for additional scientific instruments. Consequently, the fundamental problem focuses on the development of a mass spectrometric on line and *in situ* technique suitable for prospective space missions, i.e., a flexible method without time- and payload-consuming preseparation devices to quantify complex gas mixtures. Furthermore, the elucidated procedure must exclude the alteration of involved molecules and has to be capable of detecting even reactive species.

This paper presents a new approach, combining quadrupole mass spectrometry (QMS) and matrix interval algebra (MIA) to include experimental calibration errors of the mass spectrometer to resolve the chemical composition of complex gas mixtures present in, for example, planetary atmospheres, on line and *in situ*, even in the presence of thermally labile species. Additionally, this procedure can be employed for simulation chambers analyzing the interaction of cosmic ray particles or photons with frozen solids in space. This

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paper is organized as follows: Section II describes the elucidated mathematical background for extracting partial pressures of molecules in complex gas mixtures from mass spectrometric data. The performance of this approach is demonstrated explicitly by (a) generating complex, gaseous test mixtures during MeV ion bombardment of solid hydrocarbons such as CH_4, $^{13}CH_4$, and CD_4 in an ultrahigh (UHV) chamber and recording time-dependent ion currents of selected m/z values (Sec. III A), (b) the calibration procedure of the mass spectrometer (Sec. III B), and (c) resolving the composition of the mixtures performed in test experiments (Sec. IV).

II. MATHEMATICAL BACKGROUND

In the range of 10^{-4}–10^{-14} A, the QMS-probed ion current of the ith m/z value of the jth gaseous compound, I_{ij}, in a gas mixture yields the following linear relationship to the partial pressure p_j of the jth species.[5]

$$I_{ij} = p_j I_e \lambda_e \eta_{i,j} T_{ij} \sigma_{i,j} a = f_{ij} p_i \qquad (1)$$

with the electron emission current in the mass spectrometer, I_e, the mean free path of the electrons, λ_e, the ionization cross section, $\sigma_{i,j}$, the gain of the secondary electron multiplier, $\eta_{i,j}$, the transmission of the fragment, T_{ij}, and a constant a. The f_{ij} constants are determined by calibrating the mass spectrometer in respect to a gas j and its ith m/z value (see Sec. III B). Unfortunately, the measured ion current of each ith m/z value, I_i, at time t represents a sum of ion currents of this mass fragmenting from higher molecular weighted hydrocarbons and/or from parent molecules. Thus, I_i and the unknown partial pressure of the jth component p_j, holds for every element i the following linear equation:

$$I_i = \sum_j I_{ij} = \sum_j f_{ij} p_j. \qquad (2)$$

These equations form a system of j linear equations with the square calibration coefficient matrix $A = (f_{ij})$, the unknown vector of partial pressures $c = (p_j)$, and the right-hand side vector of the ion currents $b = (I_i)$. The calculation of a solution c of this system of linear equations

$$Ac = b \qquad (3)$$

is a tricky problem because calibration factors as well as ion currents are afflicted with uncertainties. The IBM product High-Accuracy Arithmetic Subroutine Library (ACRITH)[6] is an appropriate tool for solving such problems. Using a new computer arithmetic, i.e., a maximum accurate dot product and directed rounding, the methods of interval analysis,[7] and the defect correction principle,[8] an algorithmically verified result is obtained. This new arithmetic, based on the sound theory of Kulisch and Miranker,[9] uses the High-Accuracy Arithmetic Facility. This process is simulated on System/370 processors via a software package written in Assembler. ACRITH enables the user to specify the input data, including the tolerances as intervals, i.e., errors of the calibration factors (see Sec. III B) and the ion current ($\pm 1\%$). Interval arithmetic is necessary to obtain reliable and verified results. If the computed inclusion is not satisfactory, a residual correction scheme for intervals is applied to obtain an inclusion of high accuracy.[9] The algorithm implemented in ACRITH first computes an approximate inverse R of A, then a floating-point approximation of c^0. The residual iteration for the approximate solution c of the linear system (3) follows:

$$c^{k+1} = c^k + R(b - Ac^k). \qquad (4)$$

Denote the final approximation for the solution as $\tilde{c}$. Next, calculate an interval inclusion $Z = R(b - A\tilde{c})$ and the residual matrix $RA - I$ with an identity matrix. Then the interval iteration begins using $-Z = R(A\tilde{c} - b)$ as a starting point:

$$Y = Z + (RA - I)X \quad \text{with} \quad X = Y \circ \epsilon \qquad (5)$$

until Y is in X; $Y \circ \epsilon$ signifies ϵ inflation. The resulting inclusion is $\tilde{c} + Y$. The FORTRAN procedure calling for the ACRITH linear equation system solver is CALL DILINR(N, AL,AU,BL,BU,NRS,WK,CL,CU,IER), where N is the number of rows and columns, AL and AU are the lower and upper bounds of the interval matrix of the linear system, BL and BU are the lower and upper-right-hand side vectors, and CL and CU the lower and upper bounds of the result vector, respectively. The variable NRS indicates whether the linear system is to be solved with the same coefficient matrix as for the first or further right hand side, WK is the workspace vector, and IER the error code variable. The result vectors are rounded downwards and upwards. An inclusion of the solution of the linear systems (AL,AU)(CL,CU)=(BL,BU) is computed with automatic verification of the correctness of the result. (AL,AU), (CL,CU), and (BL,BU) are the intervals containing all the real matrices and vector elements for elements between AL, AU and CL, CU and BL, BU, respectively.

The solution of an interval system of linear equations (CL,CU) is the set of all solutions of any point linear system included in the interval linear system. In our problem, all calibration factors f_{ij} are afflicted with errors E_{ij}. The same coefficient matrix (AL,AU) consisting of intervals of the form $(F_{ij} - E_{ij}, F_{ij} + E_{ij})$ is chosen for all cycles. These factors are read from separate ASCII input files at the top of the program. Additionally, all ion currents I_i are measured with the same error tolerance of 1% independent of the time and the type of element. Hence, the right-hand sides are all intervals of the type $(0.99I_i, 1.01I_i)$ for each cycle, i.e., the experimental time t. The ion currents are supplied from different j ASCII files delivered from the quadrupole mass spectrometer software program. Each file contains the ion current of the jth m/z value for all cycles including background subtraction. After solving the linear equation system by selecting a corresponding set of m/z values, the interval results are stored in a file for each jth component. The program has been implemented on the IBM-Mainframe ES/9000-620 under VM/ESA of the Central Institute of Applied Mathematics of Forschungszentrum Jülich.

III. EXPERIMENT

A. On line and *in situ* generation of complex test gas mixtures

Originally, the matrix interval algebra assisted quadrupole mass spectrometry was elaborated to probe the gas phase during and after MeV ion bombardments of the frozen hydrocarbons CH_4, $^{13}CH_4$, and CD_4 in simulation experiments on the interaction of galactic cosmic ray particles with frozen matter in space.[10] To demonstrate the performance of our approach, we select two experiments, i.e., 60 min irradiation of $^{13}CH_4$ and CD_4 at 10 K with 9 MeV α particles, followed by a 60 min equilibration period, heating the samples to 70 K at 1/6 K min^{-1}, and at 1 K min^{-1} to 298 K, and keeping them for 60 min at 298. Therefore, the gas phase evolving during the irradiation and the heating period contains ion-induced, generated molecules and serves as a variable, complex, and hydrocarbon-containing test mixture.

The experimental setup is described in detail elsewhere.[10] Thus, only a brief summary is given here. The 50 ℓ vessel consists of a stainless steel chamber of 40 cm diam and 21 cm height. A programmable closed cycle helium refrigerator is attached to a differential pumped rotatable feedthrough, centered at the lid of the setup. The 10 K stage of the refrigerator holds a temperable (111) silver monocrystal serving as a substrate for condensed gases. Hydrocarbon-free UHV of $(4.2\pm0.9)\times10^{-10}$ mbar are achieved by a Drytel roughing pump operating from atmospheric pressure down to $\approx10^{-6}$ mbar and a 1500 ℓ s^{-1} cryopump.

After generating UHV conditions, $^{13}CH_4$, CH_4, or CD_4 layers, each of (5 ± 1) μm thickness, are condensed at 10^{-6} mbar onto the (10 ± 0.5) K silver substrate with the assistance of a computer-controlled thermovalve. To ensure well-defined crystal modifications, all solid hydrocarbon targets are cycled from 10 to 35 K with 0.005 K s^{-1}, annealed at 35 K for 60 min, and cooled back to 10 K with 0.005 K s^{-1}. Complex hydrocarbon mixtures are prepared by irradiating these condensates at 10 K for up to 300 min with 9 MeV α particles of the compact cyclotron CV28 in Forschungszentrum Jülich. Detailed, nonequilibrium chemistry-governed reaction pathways are elucidated.[4]

During ion bombardment and in the post-irradiation heating phase of the samples from 10 to 293 K, mass spectra from 1 to 200 amu are obtained with a Balzer QMG 420 quadrupole mass spectrometer placed 45° counterclockwise of the ion beam. The angle between the field axis, held at 5.25 V, and the silver crystal's perpendicular axis is optimized to 17.5°. Analog and digital voltages are generated by a Balzer QME 112 unit, whereas the mass analyzer consists of a Balzer QMA 120 with an axial beam source, rhenium cathode, and secondary electron multiplier operated at 1400 V. Additionally, anode and cathode potentials are refined to 150 and 60 V yielding an electron energy of 90 eV. Further on, the electron current is adjusted to (0.800 ± 0.001) mA and the electronic background signal subtracted by choosing zero mass at 5.5 amu. The scan line of the quadrupole system is calibrated at $m/z=(1.00\pm0.003)$ (H$^+$), (2.00 ± 0.01) (H$_2^+$), (12.00 ± 0.01) (C$^+$), 16.00 ± 0.02 (O$^+$,O$_2^{2+}$), (17.00 ± 0.02) (OH$^+$), (18.00 ± 0.01) (H$_2$O$^+$), (28.00 ± 0.01) (N$_2^+$, CO$^+$), (32.00 ± 0.01) (O$_2^+$), (44.00 ± 0.01) (CO$_2^+$), (61.67 ± 0.05) (^{185}Re^{3+}), (62.33 ± 0.05) (^{187}Re^{3+}), (92.50 ± 0.03) (^{185}Re^{2+}), (93.5 ± 0.03) (^{187}Re^{2+}), (185.00 ± 0.03) (^{185}Re$^+$), and (187.00 ± 0.03) (^{187}Re$^+$). All data for quantitative studies are recorded in the monitored ion detection mode, i.e., scanning time-dependent ion currents of programmed m/z values (dwell time$=1$ s amu^{-1}).

B. Determination of calibration factors of gaseous components

The calibration constants $f_{i,j}$ given in the literature [11,12] differ by up to two decades and depend strongly on the operating condition of each quadrupole mass spectrometer. Our calibration procedure does not determine absolute $f_{i,j}$ values due to the lack of a spinning rotor gauge,[13] but resolves $f_{i,j}$ by homogenizing binary gas mixtures (total pressure $p<200$ mbar) of the gas j and xenon as an internal standard in a gas mixing chamber[10] and introducing them in separate experiments at 10^{-6} mbar N$_2$-pressure equivalents into the vacuum chamber described above. This procedure yields partial pressures relative to xenon as an internal standard, hereafter designated as xenon equivalent pressures ^rp_j and relative calibration factors $F_{i,j}$. Furthermore descending a planet's atmosphere, the pressure profile is determined independently by piezo-sensors,[1] hence, justifying the introduction of xenon equivalent pressures. For $m/z=132$ of xenon, Eq. (1) yields

$$I_{132,Xe}=f_{132,Xe}\,p_{Xe} \qquad (6)$$

and

$$F_{i,j}=f_{i,j}/f_{132,Xe}=I_{ij}/I_{132,Xe}\,p_{Xe}/p_j. \qquad (7)$$

This modifies Eq. (2) to

$$I_i=\sum_j I_{ij}=\sum_j f_{ij}p_j=\sum_j F_{ij}p_j f_{132,Xe}=\sum_j F_{ij}{}^rp_j \qquad (8)$$

with a xenon equivalent pressure of the jth component ^rp_j. Obviously, relative concentrations of gases, e.g., 1 and 2 can be simply computed by dividing $^rp_1$ by $^rp_2$. Three mixtures of different gas—xenon ratios were prepared in the gas mixing chamber, introduced into the vacuum system, ion currents measured, and $F_{i,j}$ factors calculated according to Eq. (7) by averaging 20 $I_{ij}/I_{132,Xe}$—ratios of each concentration. The calibration procedure underlines an enrichment-free gas inlet in the chamber which validates Eq. (3) to $\pm0.5\%$ experimental error. Tables I–III compile m/z values and $F_{i,j}$ factors of calibrated hydrocarbons and selected residual gases including relative percentage errors.

Due to financial restrictions, neither higher molecular weighted ^{13}C- nor D-substituted hydrocarbons could be calibrated. Comparisons of identical ions of CH$_x$, ^{13}CH$_x$, and CD$_x$ fragments show a decrease of deuterated $F_{i,j}$ of between 30% and 70%, thus approximating $^DF_{i,j}=(0.5\,{}^HF_{i,j})\pm25\%$. Calibration factors for ^{13}C-labeled molecules yielded $^{13}F_{i,j}=(0.9\,{}^HF_{i,j})\pm10\%$. Additionally, the low vapor pressure of hydrocarbons restricted the calibration to masses <72 amu, cf. Table IV. The $F_{i,j}$ values of the remaining hydrocarbons were extracted from (Refs. 10 and 11) with an error limit of $\pm90\%$ as averaged over all references relevant to the operating conditions of the quadrupole mass spectrometer. The computation of integral mass

TABLE I. Calibration factors $F_{i,j}$ of hydrocarbons and selected residual gases including relative percentage errors.

m/z	nC_5H_{12}	iC_5H_{12} isopentane	iC_5H_{12} 3,3-dimethyl-propane	nC_4H_{10}	iC_4H_{10}	C_3H_8	CO_2	c-C_3H_6	n-C_3H_6
72	0.20±1	0.10±2	7.8×10^{-4}						
71	0.02±5	0.03±5	6.5×10^{-4}						
58	0.02±1	0.04±3	0.14±1	0.36±1	0.10±1				
57	0.31±5	0.96±2	3.20±1	0.06±1	0.09±1				
44	0.23±1	0.13±3	0.10±1	0.20±1	0.21±1	0.85±1	2.85±1		
43	3.60±1	2.40±3	0.21±1	3.46±1	3.71±1	0.78±1			
42	2.30±1	2.14±3	0.16±1	0.52±1	1.35±1	0.12±1		1.50±2	1.67±1
41	1.96±1	2.20±2	2.38±1	1.15±1	1.74±1	0.37±1		1.54±2	2.68±1
40	0.08±1	0.10±1	0.08±1	0.06±1	0.09±1	0.06±1		0.47±2	0.68±1
39	0.58±1	0.62±1	0.68±1	0.41±1	0.59±1	0.44±1		1.10±2	1.94±1
38	0.08±1	0.09±1	0.09±1	0.07±1	0.11±1	0.15±1		0.23±2	0.49±1
32									
30				0.04±1	0.01±1	0.07±2			
28	0.30±1	0.22±1	0.15±1	1.50±1	0.14±1	2.06±1	0.10±1	0.07±2	0.43±1
27	1.54±1	1.24±1	0.80±1	1.45±1	1.19±1	1.24±1		0.68±2	1.17±6
26	0.18±1	0.15±1	0.09±1	0.25±1	0.11±1	0.27±1		0.26±2	0.36±1
18									
16							0.41±1		
2	0.24±1	0.15±1	0.10±1	0.18±1	0.16±1	0.10±1		0.11±5	0.30±1

m/z	C_3H_4 allene	C_3H_4 propyne	O_2	C_2H_6	C_2H_4	N_2	C_2H_2	H_2O	CH_4	H_2
72										
71										
58										
57										
44										
43										
42										
41										
40	1.76± 2	2.01±1								
39	1.73± 2	1.84±1								
38	0.70± 1	0.72±1								
32			4.64±1							
30				1.87±1						
28	0.12± 2	0.11±3		7.80±1	5.86±1	8.33±1				
27	0.60± 1	0.04±1		2.37±1	3.59±1					
26	0.10± 1	0.22±1		1.70±1	3.45±1		4.10±3			
18								0.03±5		
16			0.57±1					1.3×10^{-3}	7.75±1	
2	0.25±10	0.24±3		0.18±1	0.90±1		0.34±8	0.01±10	0.07±2	11±1

spectra, i.e., recording the full mass scale (1–200 amu) by setting the digital voltage to zero, shows that less than (0.8 ±0.1)% of the subliming species hold masses >200 amu. Therefore, the mass separator is suitable for this problem.

C. Inclusion of effective pumping speed

The effective pumping speed $S_{\text{eff},j}$ of a pumping device depends on the molecular weight and—to a minor extent—on the molecular structure of the gas j. Conse-

TABLE II. Calibration factors $F_{i,j}$ and relative percentage errors of deuterated gases.

	Gas				
m/z	C_2D_6	C_2D_4	C_2D_2	CD_4	D_2
36	0.55±1				
32	3.10±1	2.01±2			
30	0.80±1	1.20±2			
28	0.66±1	1.40±2	3.10±1		
26	0.10±1	0.20±1	0.64±1		
20				5.52±1	
4	0.03±1	0.20±5	0.04±1	0.04±1	5.48±1

TABLE III. Calibration factors $F_{i,j}$ and relative percentage errors of ^{13}C-labeled gases.

	Gas			
m/z	$^{13}C_2H_6$	$^{13}C_2H_4$	$^{13}C_2H_2$	$^{13}CH_4$
32	1.60±1			
30	7.40±1	4.99±1		
28	0.07±1	3.58±1	2.80±2	
26				
17				6.77±1
14	0.07±1	0.19±3	0.20±3	0.34±2
2	0.18±1	0.79±1	0.15±3	0.06±1

TABLE IV. Experimentally noncalibrated structure classes.

Structure class	m/z (C–H)	m/z (^{13}C–H)	m/z (C–D)
Mono(di)alkyl-benzenes	$89(C_7H_5{}^+)$	$96(^{13}C_7H_5{}^+)$	$94(C_7D_5{}^+)$
Mono(di)alkyl-benzenes	$91(C_7H_7{}^+)$	$98(^{13}C_7H_7{}^+)$	$98(C_7D_7{}^+)$
Napthalene/azulene	$128(C_{10}H_8{}^+)$	$138(^{13}C_{10}H_8{}^+)$	$136(C_{10}D_8{}^+)$
Mono(di)alkyl-naphthalenes	$141(C_{11}H_9{}^+)$	$152(^{13}C_{11}H_9{}^+)$	$150(C_{11}D_9{}^+)$
Anthrazene/phenanthrene	$178(C_{14}H_{10}{}^+)$	$192(^{13}C_{14}H_{10}{}^+)$	$188(C_{14}D_{10}{}^+)$
	$177(C_{14}H_9{}^+)$	$191(^{13}C_{14}H_9{}^+)$	$186(C_{14}D_9{}^+)$
	$176(C_{14}H_8{}^+)$	$190(^{13}C_{14}H_8{}^+)$	$184(C_{14}D_8{}^+)$
1- or 2-Mono(di)alkyl-Anthrazene/phenanthrene	$191(C_{15}H_{11}{}^+)$	$\cdots$	$\cdots$
	$189(C_{15}H_9{}^+)$	$\cdots$	$\cdots$
Propane/	$\cdots$	$47(^{13}C_3H_8{}^+)/$	$52(C_3D_8{}^+)$
Propene/cyclopropene/	$\cdots/\cdots$	$45(^{13}C_3H_6{}^+)/$	$48(C_3D_6{}^+)$
Propyne/allene	$\cdots/\cdots$	$43(^{13}C_3H_4{}^+)$	$44(C_3D_4{}^+)$
Butane-isomers	$\cdot$	$62(^{13}C_4H_{10}{}^+)$	$68(C_4D_{10}{}^+)$
Pentane-isomers	$72(C_5H_{12}{}^+)$	$77(^{13}C_5H_{12}{}^+)$	$84(C_5D_{12}{}^+)$
Hexane-isomers	$86(C_6H_{14}{}^+)$	$92(^{13}C_6H_{14}{}^+)$	$100(C_6D_{14}{}^+)$
Heptane-isomers	$100(C_7H_{16}{}^+)$	$107(^{13}C_7H_{16}{}^+)$	$116(C_7D_{16}{}^+)$
Octane-isomers	$114(C_8H_{18}{}^+)$	$122(^{13}C_8H_{18}{}^+)$	$132(C_8D_{18}{}^+)$
Nonane-isomers	$128(C_9H_{20}{}^+)/$	$137(^{13}C_9H_{20}{}^+)$	$148(C_9D_{20}{}^+)$
	$127(C_9H_{19}{}^+)$		
Decane-isomers	$142(C_{10}H_{22}{}^+)/$	$152(^{13}C_{10}H_{22}{}^+)$	$164(C_{10}D_{22}{}^+)$
	$141(C_{10}H_{21}{}^+)$		
Undecane-isomers	$156(C_{11}H_{24}{}^+)$	$167(^{13}C_{11}H_{24}{}^+)$	$180(C_{11}D_{24}{}^+)$
Dodecane-isomers	$170(C_{12}H_{26}{}^+)$	$182(^{13}C_{12}H_{26}{}^+)$	$196(C_{12}D_{26}{}^+)$
Tricosane-isomers	$184(C_{13}H_{28}{}^+)$	$197(^{13}C_{13}H_{28}{}^+)$	$\cdots$
Tetracosan-isomers	$198(C_{14}H_{30}{}^+)$	$\cdots$	$\cdots$

quently, correction factors must be applied to the xenon equivalent pressure. Here, the subliming, irradiated target is defined as a leak with a leaking rate Q_j in mbar ℓ s^{-1}. The partial pressure of the jth component, p_j in mbar, the leaking rate, and the effective pumping speed hold the relation:

$$p_j S_{\text{eff},j} = Q_j. \qquad (9)$$

With a temporal constant pumping speed, the ideal gas law, and integrating over the experimental time t, the number of the jth synthesized molecule, $\#_j$, yields

$$\#_j = \frac{\int_0^t Q_j dt}{RT} \text{ const} = \frac{S_{\text{eff},j} * \int_0^t p_j dt}{RT} \text{ const} \qquad (10)$$

with const$=5.9628 \times 10^{22}$ ℓ mbar mol^{-1} J^{-1}. Equations (1)–(3), and (10) lead to the number of the jth synthesized molecules relative to xenon as an internal standard, $^r\#_j$

$$^r\#_j = \frac{S_{\text{eff},j} \int_0^t p_j^r dt}{RT} \text{ const} \qquad (11)$$

with the ideal gas constant R and the temperature T of the gas molecules. Effective pumping speeds depending on the experimental setup, e.g., conductances of the pump–chamber interfaces, the mass of the molecule, are extracted from (Ref. 14).

IV. DISCUSSION

The test experiments, i.e., the 9 MeV α-particle bombardments of frozen CH$_4$-, ^{13}CH$_4$-, and CD$_4$- targets at 10 K, are designed to demonstrate the performance of the matrix interval algebra assisted quadrupole mass spectrometry, and resolve the formation of H$_2$ and CH$_x$ ($2 \leqslant x \leqslant 3$), as well as a

great variety of higher hydrocarbons, i.e., C$_2$H$_x (2 \leqslant x \leqslant 6)$, C$_3H_x (x=4,6,8)$, C$_nH_{(2n+2)} (4 \leqslant n \leqslant 14)$, and aromatic molecules (benzene, mono- and disubstituted benzenes, naphthalenes, substituted naphthalenes, and anthracene and/or phenanthrene). A complete reaction network including formation mechanisms is elucidated.[14]

Tables V and VI quantify the generated hydrocarbons and molecular hydrogen expressed in synthesized molecules relative to xenon as an internal standard, $^r\#_j$. Although only five deuterated and four ^{13}C-labeled molecules were calibrated, reasonable error limits, suitable for planetary atmospheric research, are achieved. Furthermore, Figs. 1 and 2 depict time-dependent xenon equivalent pressures of H$_2$ during both test experiments. The relative partial pressure changes are the result of the ion bombardment (for the first 60 min) and the release to room temperature during the heating process, cf. Sec. III A. All data points and error intervals were calculated via matrix interval algebra as described in Sec. II. The computed error limits underscore the necessity for including experimental uncertainties, i.e., the ion current and the calibration. On the other hand, neglecting the errors

TABLE V. Quantification of calibrated hydrocarbons and D$_2$ in irradiated CD$_4$-targets at 10 K in terms of synthesized molecules relative to xenon as an internal standard, $^r\#_j$ [cf. Eq. (11)].

Molecule	$^r\#_j$
D$_2$	$(0.6 \pm 0.4) \times 10^{16}$
CD$_4$	$(2.3 \pm 0.4) \times 10^{18}$
C$_2$D$_2$	$(1.4 \pm 0.6) \times 10^{16}$
C$_2$D$_4$	$(1.3 \pm 0.7) \times 10^{16}$
C$_2$D$_6$	$(1.3 \pm 0.2) \times 10^{17}$

TABLE VI. Quantification of calibrated hydrocarbons and H_2 in irradiated $^{13}CH_4$ targets at 10 K in terms of synthesized molecules relative to xenon as an internal standard, $^r\#_j$ [cf. Eq. (11)]. $\Sigma^{13}C_3H_4$ defines the contributions of allene, propyne, and cyclopropene, $\Sigma^{13}C_3H_6$ those of cyclopropene and propene.

Molecule	$^r\#_j$
H_2	$(0.7\pm0.5)\times10^{18}$
$^{13}CH_4$	$(3.1\pm0.1)\times10^{18}$
$^{13}C_2H_2$	$(8.2\pm0.8)\times10^{16}$
$^{13}C_2H_4$	$(3.3\pm1.3)\times10^{15}$
$^{13}C_2H_6$	$(4.4\pm3.7)\times10^{18}$
$\Sigma^{13}C_3H_4$	$(1.4\pm0.7)\times10^{18}$
$\Sigma^{13}C_3H_6$	$(1.4\pm0.7)\times10^{18}$
$^{13}C_3H_8$	$(7.3\pm0.3)\times10^{15}$
$n\text{-}^{13}C_4H_{10}$	$(1.8\pm0.3)\times10^{15}$
$i\text{-}^{13}C_4H_{10}$	$(3.4\pm0.1)\times10^{16}$

of calibration coefficients yields, in the case of on line and *in situ* probing of complex gas mixtures, a solution of the linear equation set (3), but meaningless negative partial pressures dominate in the right-hand vector.

The data demonstrate the performance of matrix interval algebra assisted quadrupole mass spectrometry in on line and *in situ* probing of complex gas, as demonstrated in a quantification of molecular hydrogen in a complex hydrocarbon mixture. This eliminates the time- and payload-consuming preseparation techniques used in planetary space missions; calibration factors can be determined in terrestrial laboratories. In addition, a number of mixture samples from pure analytes containing neat hydrocarbons as well as oxygen, nitrogen, and other heterospecies can serve as extra checks for comparing the results of MIA and GCMS. Further on, this versatile approach can be extended to thermally labile and reactive molecules and radicals, hence, enabling one to elucidate the reactive intermediates in planetary atmospheres quantitatively. Corresponding calibration coefficients can be achieved by flash pyrolysis of radical precursors and simultaneous UV/IR–laser–QMS sampling. Therefore, matrix interval algebra assisted quadrupole mass spectrometry can replace GCMS techniques in planetary missions, if the

FIG. 2. Time-dependent xenon equivalent pressures of H_2 during a 60 min $^{13}CH_4$ irradiation at 10 K, the equilibration phase (90 min at 10 K), and during heating of the sample to 70 K at 1/6 K min^{-1}, and at 1 K min^{-1} to 298 K. The background data were collected during the first 10 min.

quantification of radicals is needed or the payload has to be reduced.

Further improvements of this procedure should focus on minimizing the experimental calibration errors: magnetic suspended, oil-free turbomolecular pumps guarantee more stable pumping speeds than a cryopump. Additionally, pumping speeds are more easily accessible through theoretical calculations because the sticking coefficients of the cold surfaces, and, in the worst case, the sublimation of gases from the first stage and the recondensation on the second one, do not have to be taken into account. Second, the operation of spinning rotor gauges[13] reduces calibration errors to less than 1%: calibration of the mass spectrometer is performed directly, i.e., without preparing binary gas mixtures. Last, the addition of higher molecular weighted hydrocarbons and their isomers elevates the level of confidence in the determination of unsaturated molecules fragmented from their parent ions.

FIG. 1. Time-dependent xenon equivalent pressures of D_2 during a 60 min CD_4 irradiation at 10 K, during the equilibration phase (90 min at 10 K), and during heating of the sample to 70 K at 1/6 K min^{-1}, and at 1 K min^{-1} to 298 K. The background data were collected during the first 10 min.

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