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MEMORANDUM

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AN APPROACH TO CONTAMINATION IDENTIFICATION

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AN APPROACH TO CONTAMINATION IDENTIFICATION

SUMMARY

A regression analysis method has been applied to unfold the waveforms resulting from complex gaseous mixtures in mass spectral analysis. The output format specifies both qualitative and quantitative chemical analysis. This method of data analysis is applied towards optical contamination identification in vacuum systems. A number of test mixtures are presented to demonstrate the feasibility of this approach. In particular, a rather difficult test case of normal butane, isobutane, and 2-cis butane is successfully analyzed.

The basic theory of analysis is discussed and the limitations inherent in regression calculations on a small computer system are indicated in a number of theoretical problems.

The equipment used only allowed this effort to be considered as a feasibility study, and the results indicate most promising analysis with research-grade instrumentation.

INTRODUCTION

Optical contamination has been arbitrarily divided into two broad categories: particulate effects and gaseous effects. The following discussion concerns gaseous contamination.

Experiments dealing with the detrimental effects of gaseous contamination quite often are accompanied by spectra resulting from either a residual gas analyzer or a mass spectrometer.

These spectra were difficult to analyze (i.e., their meaning or effect on the optical experiment). This lack of interpretation provided the motivation to determine what information could be actually derived from a mass scan and how such information might aid in eliminating those gaseous compounds that cause detrimental optical effects.

Additional incentive was supplied by the flight experiment designated T-030, which represents a flight-type quadrupole mass spectrometer with a range from 0 to 100 amu. This experiment has been suggested as a possible in situ contamination monitor to be flown in conjunction with the optical contamination experiment on board an Apollo Applications Program (AAP) mission.

STATEMENT OF THE PROBLEM

The problem of obtaining information from mass spectra was then formulated into an attempt to answer the basic question of quantitative analysis. Quantitative mass spectral analysis presents the following areas of question:

1. Qualitative — Chemical identification of compounds in an unknown spectrum
2. Quantitative analysis
    a. Relative quantitative analysis — Percent composition of each of the above compounds
    b. Absolute quantitative analysis — Partial pressure, mass or number of atoms of each of the above compounds
3. Residuals — Percent of the mixture that remains unknown after the above analysis

APPROACH TO SOLUTION OF PROBLEM

After a study of a number of texts [1, 2, 3] on mass analysis and a thorough review and exercise of mass interpretation by Wadsworth and Tunnicliff [4], a computerized multiple regression approach was adopted that was considered to be consistent with equipment available to this project.

JUSTIFICATION

The four basic assumptions in quantitative mass spectral analysis, first developed and verified by Washburn, Wiley, and Rock [5] around 1943 to 1945, are as follow:

1. Most chemical compounds in nature have their own unique set of pattern coefficients (cracking patterns). Pattern coefficients result from a normalization of the intensity at the allowed specific mass numbers for a compound (Table 1). Pattern coefficients have this unique behavior because of the nature of chemical valences and bondings existing between atoms (Table 2).

2. Pattern coefficients are stable under controlled experimental conditions. This fact is evident by how five different laboratories using different type spectrometers measured the same compound (Table 3). The degree of dissimilarity shown indicates the desirability of calibration data for a particular instrument over tabulated data in compilations such as ASTM [6] or Cornu and Massot [7].

3. The measured intensities of the ion beams of the various components in a mixture are proportional to the partial pressure of the respective components. This is because the output intensity is designed to be a linear function of the number of ions collected, and the ideal gas law is assumed valid in the pressure region where mass spectrometers work. Since pressure is the number of ions per unit volume collected multiplied by the product of Boltzmann's constant and the absolute temperature of the ions, mass spectrometers are partial pressure gauges.

4. Mixture spectra obey the principle of linear superposition. This is true because mass spectrometers are partial pressure meters, and Dalton's Law of Partial Pressure is well obeyed below 10^{-4} torr.

Dalton's law states that if several gases are present in a chamber simultaneously, the total pressure of the mixture is the sum that would be exerted if each gas were present separately. Applied to each peak in a mixture spectrum, this principle indicates that the total intensity at a specific mass value is the sum that would be measured if each gas were present separately.

DISCUSSION

A mixture spectrum at one specific mass value can mathematically be represented as a hyperplane. At all specific mass values occurring in a mixture, the problem becomes one of a set of simultaneous linear-nonhomogenous equations. In most cases, there are more equations than unknowns, the unknowns being the percentage composition of the various compounds in the mixture. The solution to such equations can be well approximated by the least squares technique of multiple linear regression [8].

Library Data

In attempting to analyze an unknown spectrum, a large library containing the pattern coefficients of pure compounds is essential. The compounds in this library are compared against the unknown. A number of logical decisions and regression calculation are performed to determine if a particular compound or group of compounds in the library belongs in the unknown mixture spectrum. This procedure is carried out until a calculated spectrum agrees favorably with the experimentally measured spectrum.

The ASTM Committee E-14 [6] and Cornu and Massot [7] libraries represent sources of vast quantities of mass spectral data. Together they contain approximately 8000 spectra. There is a great deal of duplicate spectra in these libraries. The duplications result from different laboratories contributing spectra of similar compounds. Such duplications in a library represent singularities in the mathematical analysis and were subsequently eliminated by a program designed to make these libraries unique.

Cornu and Massot data give the 10 most intense peaks per sample against 6 peaks per sample in the ASTM data. More peaks per sample tend to make a compound easier to identify by this technique. But, as indicated previously, actual calibration data of a particular instrument represent the best type of library data. The library of mass spectral data used in the ensuing analysis ranged from 100 to 1000 samples, and represents a combination of in-house calibration data with the above two sources. This library of data is stored on a magnetic disk of an IBM 1130 computer system.

In an attempt to establish the validity of the logical decisions for accepting or rejecting a library compound as existing in an unknown spectrum and simultaneously determine the effect of the regression calculations, a program for synthesizing mass spectra of mixtures was developed. A synthetic mixture by definition represents multiplying pattern coefficients of one sample by an appropriate percentage factor and adding to the pattern coefficients of another sample also multiplied by a percentage factor. In this way, 5 percent of one compound is added in the computer to 10 percent of another until 100 percent of a combination is obtained. The resulting spectrum is normalized and presented to the computer as an unknown.

Theoretical Results

This exercise indicated the theoretical limitations of the technique on an IBM 1130 system (8-k core, 0.5-million word disk storage, Table 4). Test mixture 5 represents five compounds mixed together in equal proportion. The mass range goes from 12 to 44 and contains 17 peaks. The computer program can handle up to 125 peaks. The analysis is both qualitatively and quantitatively correct. Each compound contributes 20 percent to the mixture (10 microtorr). The input, calculated and residual spectra, indicates how the calculated pattern coefficients compare to the input pattern coefficients. The residuals represent the difference between input and calculated data. If the residual contribution is above 1 percent, the residual spectrum is represented as pattern coefficients. The serial numbers associated with the compounds are for purposes of computer organization and identification on the magnetic disk.

A synthetic test mixture of eight compounds in equal proportion with 28 peaks ranging from 12 to 46 amu represented the largest mixture the IBM 1130 could handle. The qualitative analysis was correct but round-off effects resulted in 0.5-percent error in quantitative mole percentages. This round-off error results from using Gauss Jordon methods for solving the normal equations that is the heart of the regression calculations. Eight compounds in a mixture represent the maximum number that can be properly analyzed at present. To encourage these theoretical data to take on a more experimental look, deviations to the mixture spectra were added before the normalization. Another test mixture of eight in equal proportion was synthesized and a ± 3-percent deviation was added to the intensities. The mass values ranges from 12 to 75 (Table 5) containing 28 peaks. The qualitative analysis is almost correct. A 1.05 percent of butadiene appeared in the analysis, when none was actually present in the mixture. The remaining eight chemicals were properly chosen. The quantitative calculations seem reasonably accurate considering the large deviations applied to the spectrum and the round-off error in the computer. The residuals are a further effect of the large deviations. A 1-percent deviation applied to the same data and a 3-percent deviation applied to a mixture of seven compounds produced a correct analysis with very little change in the mole percentages.

The residual calculation gives an indication of how ASTM and the Cornu and Massot library are useful. Using pattern coefficients from these sources will produce contributions to the residuals and possible inaccuracy in the qualitative determination. However, allowing for such errors, the data in these tabulations save many in-house hours of calibration and can produce a reasonable analysis.

To further appreciate the significance of the residual calculations, another test was performed (Table 6), in which a mixture of five compounds in equal proportion was synthesized. Hexadiene, Serial No. 53, was eliminated from the library data. The contribution to residuals should be due entirely to the missing compound. The mole percentage for residuals was properly calculated at 20 percent, and the residual spectrum is an excellent representation of the missing compound. Residuals clearly represent deviations because of differences in calibration data and an indication of compounds not included in the library and round-off effect in the computer calculations.

The most promising aspect of this effort lies in the analysis of experimental test cases. By definition, an experimental test case represents a mixture concocted in the laboratory where mole percentages can be accurately determined.

Experimental Equipment

All test cases were measured on a Consolidated Electrodynamics Corporation Model 612 Residual Gas Analyzer. This cycloid tube [8] is not designed for analytical work, but represents a good experimental test of this technique. The instrument is specified as unit resolution at mass 44 based on a slit width of 5 mils defining the collector. Spectrum shape indicated a slit width of approximately 50 mils indicating that the spotwelded slits are missing, subsequently reducing the unit resolution to mass 20.

The reduced resolution limits the working range of the instrument to an upper limit of approximately 60 mass units (amu). The lower limit is 12, the low mass range being too unreliable for quantitative work.

Test mixtures were prepared in a glass inlet system. Quantitative mole percentages were difficult to determine because of the lack of absolute pressure calibration for the various gases used. Since this is only a feasibility study, all relative ionization probabilities for the various gases as measured by a Bayard Alpert gauge were assumed to be unity. Though this assumption is not too unreasonable for a number of gases, an undetermined error in estimated mole percentages does exist. The ion gauge was factory-calibrated only for nitrogen. All measured mole percentages are only approximate. The purpose of these experimental test mixtures is merely to indicate the feasibility of this approach.

Data were abstracted from the equipment by a two-channel analog-to-digital-to-paper-tape-to-punch cards system. As previously indicated, the entire effort is oriented around a small-size computer system. The computer generates the normalized data and calculates accurate mass numbers via standard calibration procedures and another regression technique. Background effects are eliminated by taking a scan of background prior to allowing the mixture spectrum into the spectrometer via a variable leak valve. Background and mixture data are then normalized by a factor proportional to the total number of ions collected (the total pressure). This normalization factor is effectively the sum of the area under the peaks. An approximate integration scheme is used based on constant resolution over the usable mass range and rectangular peaks. The data are now proportional to sensitivity coefficients (divisions per unit pressure), and background effects can be subtracted from the mixture gas independent of the orifice size on the variable leak.

Experimental Results

With a library of 123 compounds, a methane, CO_2, argon, neon mixture presented an excellent example of the analysis (Table 7). All of these compounds were calibrated as pure samples on the CEC 612 and included in the library data. The mass ranges from 12 to 44 including 9 peaks. These four samples represent a good degree of overlapping spectra that tends to make the analysis more difficult. The qualitative analysis is correct and the degree of agreement in the quantitative analysis is very good for a CEC 612 RGA. The indication of approximately known mole percentages is because of reading pressure valves on an ion gauge only calibrated for nitrogen.

With 12 peaks ranging from 12 to 45, the methane, nitrogen, carbon dioxide, neon, oxygen, argon represents an abundance of overlapping spectra. This mixture of six compounds (Table 8) represents a very difficult case to interpret. The qualitative analysis is correct, choosing the proper six from a library of 150 compounds. All of the compounds in this mixture except oxygen represent in-house calibration data. For such a complex mixture, the quantitative analysis is very encouraging.

The normal butane, isobutane, 2-cis butane (Table 9) represents the most difficult experimental test case successfully analyzed to date. Normal butane and isobutane have very similar pattern coefficients with common base peaks at 43 amu. The degree of overlapping spectra and the abundance of compounds in this region tend to make the analysis very difficult. There are 18 peaks with mass ranges of 13 to 58. Each of these spectra was individually calibrated on the CEC 612. With a library of about 150 compounds the analysis took about 90 seconds. The degree of agreement seems very favorable.

Additional experimental test mixtures are included in Appendix A.

FUTURE EFFORT

The opportunity to gather an abundance of information from the residual gas analyzer has recently been made available. A seven-channel analog tape with appropriate operational amplifiers on each channel is being prepared to read various signals from the spectrometer. A DDP-116 will convert this information to a digital signal. This future effort is aimed at improved quantitative analysis by having more reliable and accurate data. Applying some wave-shape considerations coupled with the instrument resolution (polynomial regression and multiparameter optimization techniques) should allow for accurate location of spectral position and intensity.

The multichannel information should also allow for normalization of temperature variations, pressure excursions, amplifier drift, control voltage, and current instabilities. This normalization should improve the stability of the data.

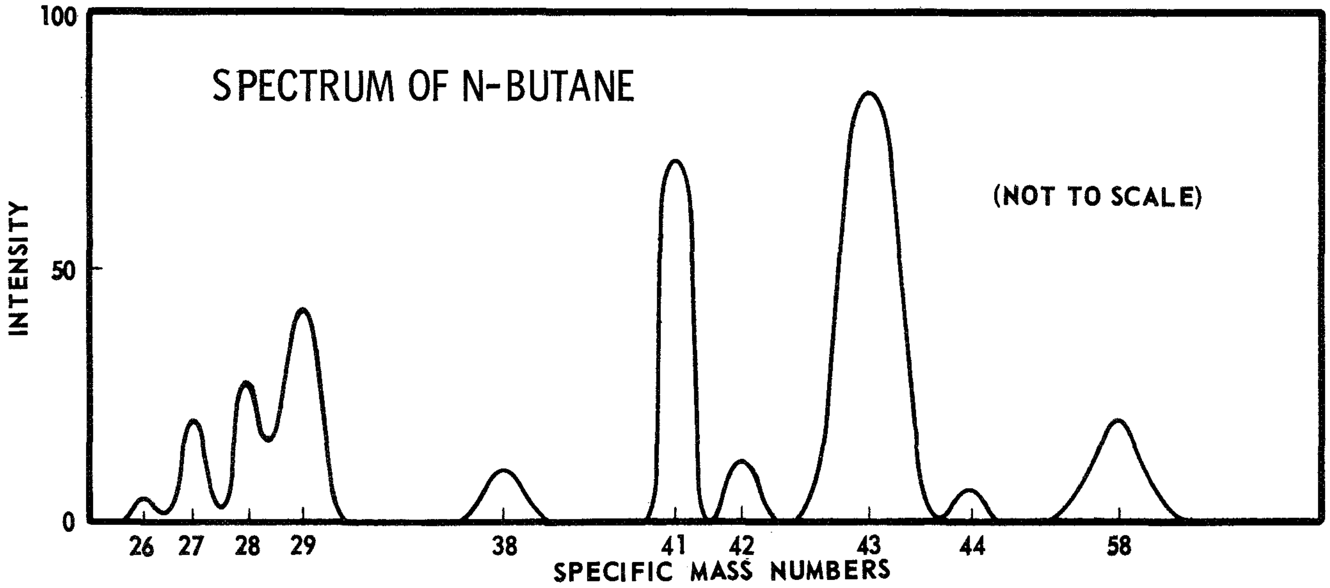
At the heart of the regression calculations, a symmetric coefficient matrix is effectively being inverted. A number of techniques exist for solutions of simultaneous equations that result in better accuracy than Gauss-Jordan. Some of these techniques are presently being pursued and more complex test cases are being attempted.

CONCLUSION

In conclusion, this effort applied to T-030 allows an ability to interpret the data sent back from the quadrupole mass spectrometer. This interpretation of the data should aid in understanding the ambient atmosphere of the spacecraft, and increase the probability of detecting detrimental contaminants.

There also appears to be an excellent opportunity to apply this technique as an aid to the experimentalist concerned with the ambient atmosphere surrounding optical contamination experiments.

TABLE 1. MASS SPECTRAL DATA FOR N-BUTANE



TABULATED DATA

MASS NUMBER	INTENSITY (ARBITRARY UNITS)	PATTERN COEFFICIENTS (% BASE PEAK)
26	1.93	2.50
27	17.45	22.50
28	19.00	24.50
29	25.98	33.50
38	6.98	9.00
41	20.16	86.00
42	10.00	13.00
43	77.54	100.00 BASE PEAK
44	2.72	3.50
58	12.79	10.50

TABLE 2. MASS SPECTRAL DATA PATTERN COEFFICIENTS

M/E	METHANE	AMMONIA	WATER	NEON	NITROGEN	ETHANE	METHANOL	PROPANE	M/E
1	3.10								1
12	2.50								12
13	8.00								13
14	16.00	2.00			5.00	1.00			14
15	85.00	7.50				2.00			15
16	100.00	80.00							16
17		100.00	21.00						17
18			100.00						18
20				100.00					20
22				10.00					22
25						2.00			25
26						18.00		5.00	26
27						29.00		31.50	27
28					100.00	100.00	33.00	61.50	28
29						23.50	100.00	100.00	29
30						30.00	66.00		30
31							3.00		31
38								4.00	38
39								16.50	39
41								14.60	41
42								6.00	42
43								33.50	43
44								40.00	44

TABLE 3. SIMILARITIES IN PATTERN COEFFICIENTS N-BUTANE

M/E	I	II	III	IV	V
15			5.00	2.00	
26		2.50	6.00		4.00
27	24.00	22.50	37.00	31.00	28.10
28	27.50	24.50	32.50	29.50	27.10
29	37.50	33.50	44.00	41.00	38.00
39	12.00	9.00	12.50	11.00	10.50
41	33.00	20.00	27.50	27.60	27.50
42	16.00	13.00	12.00	11.00	11.50
43	100.00	100.00	100.00	100.00	100.00
44	3.50	3.50			3.00
52				2.50	
57	3.50				
58	27.00	16.50	12.00	20.10	11.00

PATTERN COEFFICIENTS AS MEASURED BY FIVE DIFFERENT LABORATORIES.

TABLE 4. SYNTHETIC SAMPLE TEST MIXTURE 5

INPUT SAMPLE TEST MIXTURE 5 20% 60, 232, 1595, 1592, 11

SERIAL NUMBER	COMPOUND NAME OR FORMULA	PARTIAL PRESSURE (MICRO-TORR)	MOLE PERCENTAGE
60	METHANE	10.00	20.00
232	WATER	10.00	20.00
1595	NITROGEN	10.00	20.00
1592	OXYGEN	10.00	20.00
11	ARGON	10.00	20.00

TOTAL PRESSURE OBSERVED
50.00

SPECTRAL PATTERNS

M/E	INPUT	CALCULATED	RESIDUAL	M/E
12	0.76	0.76	-0.00	12
13	2.77	2.77	-0.00	13
14	12.15	12.15	-0.00	14
15	72.15	72.17	-0.01	15
16	100.00	100.02	-0.02	16
17	21.33	21.34	-0.00	17
18	95.69	95.71	-0.02	18
19	0.47	0.47	-0.00	19
20	14.25	14.26	-0.00	20
28	96.07	96.10	-0.02	28
29	0.66	0.67	-0.00	29
33	0.00	0.00	0.00	33
34	0.09	0.09	-0.00	34
36	0.28	0.28	-0.00	36
38	0.09	0.09	-0.00	38
40	95.69	95.71	-0.02	40
44	0.00	0.00	0.00	44

RMS RESIDUALS
0.357E-01

TABLE 5. SYNTHETIC SAMPLE TEST MIXTURE 8

INPUT SAMPLE TEST MIXTURE 8 12.5% 17, 21, 31, 53, 82, 100, 107, 123 ±3%DEV TEMP - 22.5°C

SERIAL NUMBER	COMPOUND NAME OR FORMULA	PARTIAL PRESSURE (MICRO-TORR)	MOLE PERCENTAGE
17	CARBON MONOXIDE	6.303	12.61
21	PROPANOIC ACID	6.023	12.05
31	ETHYLAMINE	6.999	14.00
53	HEXADIENE	5.557	11.11
82	NITROUS OXIDE	6.193	12.39
96	BUTADIENE	0.525	1.05
100	HEXANE	3.737	7.47
107	SULFUR DIOXIDE	6.416	12.83
123	THIOPHENE	5.027	10.05
	RESIDUALS	3.219	6.44
		TOTAL PRESSURE OBSERVED	
		50.000	

TABLE 6. SYNTHETIC SAMPLE TEST MIXTURE 5

INPUT SAMPLE	TEST MIXTURE 5 20%17, 21, 31, 53, 82	(53 ELIMINATED)	TEMP - 22.5°C
SERIAL NUMBER	COMPOUND NAME OR FORMULA	PARTIAL PRESSURE (MICRO-TORR)	MOLE PERCENTAGE
17	CARBON MONOXIDE	9.159	18.32
21	PROPANOIC ACID	10.742	21.48
31	ETHYLAMINE	10.250	20.50
82	NITROUS OXIDE	9.864	19.73
	RESIDUALS	9.985	19.97
		TOTAL PRESSURE OBSERVED 50.000	

SPECTRAL PATTERNS

M/E	INPUT	CALCULATED	RESIDUAL	M/E
29.0	100.00	99.97	0.05	28.0
12.0	2.08	1.91	0.41	12.0
16.0	2.91	2.82	0.22	16.0
29.0	35.41	38.03	-6.28	29.0
14.0	5.83	5.73	0.23	14.0
30.0	55.00	55.91	-2.19	30.0
74.0	32.50	34.96	-5.91	74.0
27.0	42.91	33.35	22.95	27.0
45.0	31.66	33.64	-4.73	45.0
73.0	20.00	21.51	-3.63	73.0
44.0	50.00	49.71	0.67	44.0
18.0	5.41	5.56	-0.34	18.0
41.0	41.66	0.00	100.00	41.0
67.0	34.16	0.00	82.00	67.0
39.0	25.41	0.00	61.00	39.0
54.0	22.08	0.00	53.00	54.0
53.0	4.16	0.00	10.00	53.0

BASE PEAK = 0.4166E 02

TABLE 7. EXPERIMENTAL SAMPLE — CO_2/METHANE/ARGON/NEON

```
INPUT SAMPLE      CO2/METHANE/ARGON/NEON     40/29/18/13            TEMP -  22.5°C
SERIAL NUMBER       COMPOUND NAME OR FORMULA       PARTIAL PRESSURE     MOLE PERCENTAGE
                                                    (MICRO-TORR)       CAL.    APPROX.
     4              METHANE                            0.363           19.11    29.00
     7              NEON                               0.422           22.19    13.00
    46              ARGON                              0.279           14.69    18.00
    81              CARBON DIOXIDE                     0.807           42.46    40.00
                    RESIDUALS                          0.029            1.55
                                              TOTAL PRESSURE OBSERVED
                                                       1.899
                                 SPECTRAL PATTERNS

                   INPUT          CALCULATED          RESIDUAL
            M/E                                                          M/E
            12.0        5.53          6.89             -37.22            12.0
            13.0        3.01          3.14              -3.70            13.0
            14.0        0.85          4.49            -100.00            14.0
            15.0       43.02         41.81              33.18            15.0
            16.0       48.23         48.96             -19.86            16.0
            20.0       52.13         52.22              -2.48            20.0
            22.0        7.47          6.56              24.90            22.0
            40.0       34.55         34.56              -0.24            40.0
            44.0      100.00         99.89               2.77            44.0
                                        BASE PEAK = 0.3646E 01
```

TABLE 8. EXPERIMENTAL SAMPLE — METHANE/N_2/CO_2/Ne/O_2/ARGON

INPUT SAMPLE METH/N2/C02/NE/02/AR 30/28/20/13/7/2 TEMP - 22.5°C

SERIAL NUMBER	COMPOUND NAME OR FORMULA	PARTIAL PRESSURE (MICRO-TORR)	MOLE PERCENTAGE CAL.	MOLE PERCENTAGE APPROX.
4	METHANE	0.949	36.51	30.00
7	NEON	0.246	9.47	13.00
13	NITROGEN	0.609	23.42	28.00
45	OXYGEN	0.057	2.20	7.00
46	ARGON	0.060	2.32	2.00
81	CARBON DIOXIDE	0.532	20.44	20.00
	RESIDUALS	0.147	5.64	

TOTAL PRESSURE OBSERVED
2.600

SPECTRAL PATTERNS

M/E	INPUT	CALCULATED	RESIDUAL	M/E
12.0	3.00	5.38	-15.35	12.0
13.0	7.20	7.03	1.14	13.0
14.0	28.76	13.26	100.00	14.0
15.0	94.97	93.40	10.17	15.0
16.0	100.00	102.98	-19.23	16.0
20.0	25.95	26.05	-0.65	20.0
22.0	4.23	3.23	6.50	22.0
28.0	63.81	64.58	-4.99	28.0
32.0	6.21	6.04	1.11	32.0
40.0	6.37	6.38	-0.06	40.0
44.0	56.48	56.23	1.62	44.0
45.0	0.53	0.56	-0.15	45.0

BASE PEAK = 0.1550E 02

TABLE 9. EXPERIMENTAL SAMPLE — N-BUTANE/2 BUTENE CIS/ISOBUTANE

INPUT SAMPLE N BUTANE / 2 BUTENE CIS / ISOBUTANE 38/33/29 TEMP - 22.5°C

SERIAL NUMBER	COMPOUND NAME OR FORMULA	PARTIAL PRESSURE (MICRO-TORR)	MOLE PERCENTAGE	APPROX.
1349	2 BUTENE CIS	1.304	25.08	33
10594	NORMAL BUTANE	2.480	47.70	38
23971	ISOBUTANE	1.142	21.96	29
	RESIDUALS	0.274	5.27	
		TOTAL PRESSURE OBSERVED 5.199		

APPENDIX A

TABLE A-1. EXPERIMENTAL SAMPLE — N-BUTANE/ISOBUTANE

INPUT SAMPLE N BUTANE/ISOBUTANE 50/50 TEMP - 22.5°C

SERIAL NUMBER	COMPOUND NAME OR FORMULA	PARTIAL PRESSURE (MICRO-TORR)	MOLE PERCENTAGE CAL.	MOLE PERCENTAGE APPROX.
39	ISOBUTANE	4.999	62.49	50.00
57	NORMAL BUTANE	2.829	35.36	50.00
	RESIDUALS	0.172	2.15	

TOTAL PRESSURE OBSERVED
7.999

SPECTRAL PATTERNS

M/E	INPUT	CALCULATED	RESIDUAL	M/E
15.0	3.75	5.73	-90.91	15.0
27.0	23.74	21.55	100.00	27.0
29.0	16.66	18.49	-83.85	29.0
32.0	0.35	0.00	16.39	32.0
37.0	1.45	1.08	17.31	37.0
38.0	2.21	1.90	14.06	38.0
39.0	13.75	14.82	-48.74	39.0
41.0	39.58	40.65	-48.55	41.0
42.0	21.70	21.59	5.09	42.0
43.0	100.00	99.48	23.52	43.0
50.0	0.67	0.00	30.99	50.0
53.0	0.00	0.00	0.02	53.0
57.0	2.70	1.58	50.89	57.0
58.0	2.50	2.12	17.52	58.0

BASE PEAK = 0.2186E 01

TABLE A-2. EXPERIMENTAL SAMPLE — ARGON/NEON/CO_2

INPUT SAMPLE ARGON/NEON/CO2 33/33/33 TEMP - 22.5°C

SERIAL NUMBER	COMPOUND NAME OR FORMULA	PARTIAL PRESSURE (MICRO-TORR)	MOLE PERCENTAGE	
			CAL.	APPROX.
7	NEON	0.526	32.87	33.00
35	ARGON	0.616	38.48	33.00
49	CARBON DIOXIDE	0.459	28.66	33.00

TOTAL PRESSURE OBSERVED
1.600

SPECTRAL PATTERNS

M/E	INPUT	CALCULATED	RESIDUAL	M/E
12.0	3.08	4.54	-1.45	12.0
20.0	85.53	85.40	0.12	20.0
22.0	9.99	11.23	-1.24	22.0
40.0	100.00	99.98	0.01	40.0
44.0	74.58	74.47	0.10	44.0
45.0	1.04	0.74	0.30	45.0

RMS RESIDUALS = 0.795E 00

TABLE A-3. EXPERIMENTAL SAMPLE — KD RUDOLPH

```
INPUT SAMPLE   TEST MIXTURE  KD  RUDOLPH                                TEMP-  22.5°C

SERIAL NUMBER    COMPOUND NAME OR FORMULA    PARTIAL PRESSURE     MOLE PERCENTAGE
                                               (MICRO-TORR)·       CAL.    KNOWN

      1          HYDROGEN                        0.158             3.41
     29          NITROGEN                        4.286            95.14   100.00
     95          ARGON                           0.070             1.45
                                           TOTAL PRESSURE OBSERVED
                                                 4.500


                              SPECTRAL PATTERNS

                    INPUT        CALCULATED       RESIDUAL

          M/E                                                      M/E
          2.0        3.60           3.60            0.00           2.0
         14.0       15.60           5.12           10.47          14.0
         28.0      100.00         100.53           -0.53          28.0
         40.0        1.53           1.53            0.00          40.0

                                   RMS RESIDUALS=  0.524E 01
```

TABLE A-4. EXPERIMENTAL SAMPLE — AIR

```
INPUT SAMPLE    AIR                                                       TEMP-    22.5°C

SERIAL NUMBER   COMPOUND NAME OR FORMULA      PARTIAL PRESSURE     MOLE PERCENTAGE
                                                (MICRO-TORR)       CAL.      KNOWN

      29        NITROGEN                          5.967            63.36     80.00
      83        OXYGEN                            2.010            21.31     19.00
      95        ARGON                             0.342             3.59      1.00
                RESIDUALS                         1.109            11.74
                                          TOTAL PRESSURE OBSERVED
                                                  9.410


                              SPECTRAL PATTERNS

                   INPUT       CALCULATED       RESIDUAL

            M/E                                                M/E
            14.0    23.85         5.14            100.00       14.0
            28.0   100.00       100.00             -5.09       28.0
            29.0     1.17         0.00              6.27       29.0
            32.0    33.95        33.95              0.00       32.0
            40.0     5.71         5.71              0.00       40.0

                                          BASE PEAK=  0.1870E 02
```

TABLE A-5. EXPERIMENTAL SAMPLE — METHANE/NEON

INPUT SAMPLE METHANE NEON MIXTURE 50/50 TEMP - 22.5°C

SERIAL NUMBER	COMPOUND NAME OR FORMULA	PARTIAL PRESSURE (MICRO-TORR)	MOLE PERCENTAGE
24073	METHANE	0.185	74.13
12059	NEON	0.058	23.12
	RESIDUALS	0.007	2.74
		TOTAL PRESSURE OBSERVED 0.250	

SPECTRAL PATTERNS

M/E	INPUT SPECTRUM	CALCULATED SPECTRUM	RESIDUAL SPECTRUM	M/E
12.0	0.16	2.16	-54.90	12.0
13.0	6.63	7.19	-15.23	13.0
14.0	13.50	9.85	100.00	14.0
15.0	89.79	91.65	-50.93	15.0
16.0	100.00	98.55	39.68	16.0
20.0	30.77	30.74	0.97	20.0
21.0	2.22	0.00	61.05	21.0
22.0	2.85	3.19	-9.37	22.0
27.0	0.18	0.00	4.96	27.0
43.0	0.38	0.00	10.54	43.0

BASE PEAK = 0.3646E 01

TABLE A-6. EXPERIMENTAL SAMPLE — NEON/CO_2

```
INPUT SAMPLE   NEON  CO2 MIXTURE  NE  80   CO2  20                  TEMP -  22.5°C

SERIAL NUMBER    COMPOUND NAME OR FORMULA    PARTIAL PRESSURE    MOLE PERCENTAGE
                                               (MICRO-TORR)

   12059         NEON                             4.393               87.87
   21907         CARBON DIOXIDE                   0.607               12.13
                                          TOTAL PRESSURE OBSERVED
                                                  5.000


                              SPECTRAL PATTERNS

          INPUT SPECTRUM     CALCULATED SPECTRUM      RESIDUAL SPECTRUM
M/E                                                                       M/E
12.0           0.36                0.85                   -0.49           12.0
20.0         100.00               99.99                    0.00           20.0
21.0           0.31                0.00                    0.31           21.0
22.0          10.66               10.66                   -0.00           22.0
40.0           0.49                0.00                    0.49           40.0
44.0          13.84               13.81                    0.02           44.0
45.0           0.19                0.13                    0.05           45.0

                                     RMS RESIDUALS =  0.291E  00
```

TABLE A-7. EXPERIMENTAL SAMPLE — CO_2/METHANE/NEON

INPUT SAMPLE CO2/METHANE/NEON 40/30/30 TEMP - 22.5°C

SERIAL NUMBER	COMPOUND NAME OR FORMULA	PARTIAL PRESSURE (MICRO-TORR)	MOLE PERCENTAGE CAL	MOLE PERCENTAGE KNOWN
24073	METHANE	0.470	13.06	~30.00
12059	NEON	1.443	40.09	~30.00
21907	CARBON DIOXIDE	1.611	44.75	~40.00
	RESIDUALS	0.075	2.09	

TOTAL PRESSURE OBSERVED
3.599

SPECTRAL PATTERNS

M/E	INPUT SPECTRUM	CALCULATED SPECTRUM	RESIDUAL SPECTRUM	M/E
12.0	4.80	6.83	-43.45	12.0
13.0	1.84	2.12	-5.96	13.0
14.0	5.28	2.91	50.77	14.0
15.0	27.80	27.10	14.98	15.0
16.0	32.71	33.54	-17.62	16.0
20.0	89.35	89.45	-2.19	20.0
22.0	12.18	11.20	21.14	22.0
27.0	4.66	0.00	100.00	27.0
32.0	0.14	0.00	3.19	32.0
40.0	0.98	0.00	21.11	40.0
44.00	100.00	99.85	3.06	44.0

BASE PEAK = 0.4661E 01

TABLE A-8. EXPERIMENTAL SAMPLE — TEST

INPUT SAMPLE TEST

TEMP- 22.5°C

SERIAL NUMBER	COMPOUND NAME OR FORMULA	PARTIAL PRESSURE (MICRO-TORR)	MOLE PERCENTAGE CAL.	KNOWN
29	NITROGEN	4.675	73.33	68.24
83	OXYGEN	0.877	13.70	18.00
95	ARGON	0.376	5.83	3.18
	RESIDUALS*	0.460	7.14	8.36
		TOTAL PRESSURE OBSERVED 6.370		

SPECTRAL PATTERNS

M/E	INPUT	CALCULATED	RESIDUAL	M/E
14.0	13.36	5.12	84.26	14.0
20.0	1.09	1.15	-0.59	20.0
28.0	100.00	100.42	-4.29	28.0
32.0	18.76	18.76	0.00	32.0
40.0	7.98	7.98	0.08	40.0
44.0	9.78	0.00	100.00	44.0

BASE PEAK= 0.9783E 01

* RESIDUALS= 4.90% HELIUM, 3.40% HYDROGEN.

TABLE A-9. EXPERIMENTAL SAMPLE — N_2/NEON/CO_2/METHANE/ARGON

INPUT SAMPLE SERIAL NUMBER	N2/NE/CO2/METH/AR 28/26/22/22/2 COMPOUND NAME OR FORMULA	PARTIAL PRESSURE (MICRO-TORR)	TEMP - 22.5°C MOLE PERCENTAGE CAL.	KNOWN
4	METHANE	0.955	25.14	22.00
7	NEON	1.490	39.21	26.00
46	ARGON	0.260	6.84	2.00
81	CARBON DIOXIDE	1.062	27.94	22.00
	RESIDUALS	0.029	0.87	

TOTAL PRESSURE OBSERVED
3.800

SPECTRAL PATTERNS

M/E	INPUT	CALCULATED	RESIDUAL	M/E
12.0	3.67	5.56	-84.23	12.0
13.0	4.58	4.49	3.95	13.0
14.0	5.25	6.41	-52.01	14.0
15.0	61.92	59.68	100.00	15.0
16.0	65.09	67.02	-86.38	16.0
20.0	100.00	100.11	-5.11	20.0
22.0	12.04	10.89	51.23	22.0
40.0	17.45	17.46	-0.51	40.0
44.0	71.50	71.32	7.99	44.0

BASE PEAK = 0.2238E 01

TABLE A-10. EXPERIMENTAL SAMPLE — CO_2/N-BUTANE/ARGON

CO2/N BUTANE/ARGON 30/30/30

TEMP - 22.5°C

INPUT SAMPLE SERIAL NUMBER	COMPOUND NAME OR FORMULA	PARTIAL PRESSURE (MICRO-TORR)	MOLE PERCENTAGE CAL.	MOLE PERCENTAGE KNOWN
7	NEON	0.132	4.11	
35	ARGON	1.402	43.83	40.00
43	N BUTANE	0.574	17.94	30.00
49	CARBON DIOXIDE	1.043	32.59	30.00
	RESIDUALS	0.049	1.53	

TOTAL PRESSURE OBSERVED

3.200

SPECTRAL PATTERNS

M/E	INPUT	CALCULATED	RESIDUAL	M/E
12.0	3.84	4.53	-19.78	12.0
20.0	9.58	9.37	5.88	20.0
22.0	1.40	3.40	-57.14	22.0
26.0	2.42	1.63	22.55	26.0
27.0	14.95	11.46	100.00	27.0
29.0	17.83	15.55	65.19	29.0
39.0	3.53	4.29	-21.82	39.0
40.0	100.00	99.97	0.62	40.0
41.0	13.52	11.25	65.04	41.0
42.0	4.35	4.70	-10.09	42.0
43.0	38.86	40.93	-59.47	43.0
44.0	75.64	75.57	2.08	44.0
45.0	1.25	0.74	14.76	45.0
58.0	1.74	4.50	-79.06	58.0

BASE PEAK = 0.3489E 01

TABLE A-11. EXPERIMENTAL SAMPLE — AMMONIUM HYDROXIDE

INPUT SAMPLE SERIAL NUMBER	AMMONIUM HYDROXIDE NH4OH 29 & H20 71 COMPOUND NAME OR FORMULA	PARTIAL PRESSURE (MICRO-TORR)	TEMP - 22.5°C MOLE PERCENTAGE
5	AMMONIA	1.967	24.89
6	WATER	5.185	65.64
46	ARGON	0.256	3.24
	RESIDUALS	0.492	6.23

TOTAL PRESSURE OBSERVED
7.900

SPECTRAL PATTERNS

M/E	INPUT	CALCULATED	RESIDUAL	M/E
14.0	0.75	0.75	-0.07	14.0
15.0	0.96	3.03	-21.79	15.0
16.0	29.89	39.39	-100.00	16.0
17.0	66.77	59.00	81.79	17.0
18.0	100.00	100.50	-5.34	18.0
19.0	0.64	5.00	-45.90	19.0
20.0	1.29	3.00	-18.03	20.0
40.0	4.94	4.94	0.00	40.0

BASE PEAK = 0.9500E 01

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