Analytical Errors in Routine Gas Chromatography Analysis

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Conducting the analysis of trace-level impurities in high purity gases by gas chromatography technique could be a real challenge. This is because the several possible sources of analytical errors which may occur in daily operation. These errors may include contamination, measurement errors and mechanical/instrument errors. This work assesses possible contamination situations of the analyte gas caused by pressure reducers. The influence on the measurements by gas chromatography (GC) is highlighted in two practical situations, i) first, with impurities such as oxygen (O_2) and nitrogen (N_2) from atmospheric air, and ii) second, with carbon dioxide (CO_2) from previous analysis. The solutions are also presented and experimentally proven, so that the problems to be avoided and to achieve reproducible results, to shorten the analysis time and to extend the lifetime of GC separation columns.

Keywords: gas chromatography, analytical errors, routine analysis

According to their grade of purity, several applications of gases are found both in research and industry, including in high precision analytical testing. Therefore, establishing the level of gas purity represents a critically important criterion having significant impact to the price/quality ratio.

Particularly, for oxygen and nitrogen as major constituents of atmospheric air, their determination as trace level impurities is of strong interest to the analytical community due to the influence that may have on the results of gas analysis [1].

The most common method and, in the same time, one of the most complex for the identification and quantification of impurities in different gases is the gas chromatography (GC). During the last decade, GC has become a reliable analytical technique. According to the analytes and their quantity in the sample, this method can be configured using different chromatographic stationary phases and detectors. Oxygen and nitrogen can be well separated using molecular sieve columns (stationary phase), while carbon dioxide, water and other polar compounds can be separated using Q-plot polymer columns [1-7].

Thermal conductivity detector (TCD) is typically used to measure nitrogen, oxygen, carbon dioxide, carbon monoxide and light hydrocarbons, instead flame ionization detector (FID) is used for the determination of higher hydrocarbons, but also for the quantification of carbon monoxide and carbon dioxide, only if these components are previously converted in methane by a nickel-based methanizer [2, 8-11].

Gas chromatography with pulsed discharge helium ionization detector (PDHID), described as an analytical technique with universal detection capability and high sensitivity for permanent gases, is commonly used to detect trace levels of impurities in high purity bulk gases, as well as organic compounds ranging from light hydrocarbons to high molecular weight pesticides and metal complexes [12-20]. PDHID has an advantage over flame ionization detector (FID), where permanent gases like oxygen and nitrogen give little or no response. Also, it is three orders of magnitude more sensitive than thermal conductivity detection (TCD) [21-25]. Its background current is significantly affected by the purity of the carrier gas and it is sensitive to any contaminant [26, 27].

Possible sources of analytical errors could appear during the gas chromatography analysis. These errors may include contamination, measurement errors and instrumental errors [28-351].

A critical issue in GC analysis is that a wrong interpretation of the data could lead to false results. The most frequent problem that could occur in GC analysis is the contamination of the sample. This can be a consequence of gas leaks due to mounting, poor seals or other auxiliary components that come in contact with sample, as the cylinder pressure reducer.

In one of their research works, Janse van Rensburg, Botha and Rohwerb observed that the sample inlet pressure had an effect on the amount of oxygen leaking into the system from the air [1]. They expected to have small leaks because the gas chromatograph used for experiments was equipped with valves that were not helium-purged. After some tests, Janse van Rensburg et al. have shown that the oxygen leaking into the system is diminished with the increase of the sample flow rate from 25 mL/min to 100 mL/min.

Other researchers revealed the advantages of a special configuration of gas chromatographic system, consisting in a serially connection of two planar microfluidic devices, three-port endowed, having built-in fluidic gates and a mid-point pressure source. They developed and implemented a specific analysis for the measurement of oxygen, nitrogen, carbon monoxide, carbon dioxide and light hydrocarbons in a single step [2]. This approach eliminates many chromatographic issues encountered with column connectivity and the use of multi-port valves, where permanent plumbing is required.

From our knowledge there are no published studies specific on the issue of sample contamination with residual

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impurities from the cylinder pressure reducer, reason for this paper to present some examples of possible contamination caused by these auxiliary components used in the analytical testing/certification of gases and the solutions to avoid them. These problems could occur in any gas chromatographic method where the pressure reducers are used to reduce and adjust the pressure of a sample from cylinder.

Experimental part

Gas chromatography system

All the experiments were performed on a Bruker Scion 456 Gas Chromatograph (Bruker Chemical Analysis, Netherlands) with MS Workstation 8 software (Bruker Daltonik GmbH, Germany). The GC system was equipped with two pulsed discharge helium ionization detectors (PDHID), a sample admission valve (on-off valve), a split injection valve and a column selection valve. The valves were purged with the same purity helium (6.0 grade) as the carrier gas.

The separation columns (Bruker Daltonics Inc., United States) were selected according to the properties of the gases to be measured. The first column was a Bruker BR-Q-PLOT (divinylbenzene PLOT column) with dimensions 30 m x 0.53 mm internal diameter, which was used to separate carbon dioxide from the oxygen and nitrogen (air). The second column was a Bruker BR-Molsieve 5A (molecular sieve 5 Å PLOT column) with dimensions 30 m x 0.53 mm internal diameter. This column was used to separate nitrogen, oxygen from the bulk gas. VICI Valco Cheminert removable fused silica adapters were used to adapt the column diameter to the 1/16 in. nut fittings that connected the column to the valve and to the detector inlet. Stainless steel tubing was used throughout the sampling system and connections were tested for integrity by pressurizing the system with helium and testing for leaks with an electronic leak detector (Edwards - Gas Check B4, United Kingdom).

A Dell Vostro desktop computer (Dell Inc., United States) equipped with a Pentium Core-I3 1.7 GHz processor, 3 gigabytes of RAM, and 500 Gb hard drive with Windows 7 (Microsoft Corporation, Romania) as operating system was used to host the software and process the data obtained.

Samples and materials

The samples, purchased from Messer Romania Gaz, were two gas materials with known composition: 2.1 ppm O_2, 35.0 ppm N_2 in H_2 and 1.3 ppm CO_2 in N_2. Prior to the experiments, the impurities from the gas samples were confirmed in-house by mass spectrometry method using a VG Prolab Advanced (Thermo Electron Corporation, United Kingdom). To establish and to control the sample flow from the cylinders through the sample loop of the GC, two-stage reducers with stainless steel membranes purchased from Linde Gaz Romania were used.

The carrier gas (Helium 6.0 grade), the valve actuator gas (air) and the gas standards (3.2 ppm O_2, 2.8 ppm N_2, 3.1 ppm CO_2 in He; 30.5 ppm O_2, 30.3 ppm N_2, 28.9 ppm CO_2 in He, 150.1 ppm O_2, 149.3 ppm N_2, 148.8 ppm CO_2 in He and 299.1 ppm O_2, 300.4 ppm N_2, 301.1 ppm CO_2 in He) were purchased from Messer Romania Gaz.

Experiment procedure

To demonstrate the possible contamination of gas sample caused by the pressure reducers, the samples were analysed both without and with purge of pressure reducers.

Prior to the experiments, using the operating software (MS Workstation 8), the sample admission valve was set on closing position (OFF position) and the sample loop was purged with Helium 6.0 grade, used also as carrier gas. After five minutes, the gas from sample loop was injected and analysed. This procedure has been performed to eliminate the possible impurities from sample loop or columns and to verify whether it occurs the diffusion of air into the sample or carrier stream (through small leaks).

The experiment was carried out isothermally at 40°C. The detectors were set at 110°C. Injection volume was 30 μL and a split ratio of 1:1 was employed.

Results and discussions

Figure 1 and figure 2 presents the chromatograms obtained on Molsieve 5A, respectively Q-Plot columns, which results after the analysis of the purge gas over 2 runs. As it can be observed in figure 1, the O_2 and N_2 peaks are under the detection limit (L_D=0.5 ppm). It means that the diffusion of air into the system path does not occur.

As it may be noticed from figure 2, in the chromatograms resulted on Q-Plot column no CO_2 peak was detected, it can only be observed an increase of baseline caused by the switching of column selection valve, which resulted in disturbance of gas flow.

After 7 injections of the sample containing 2.1 ppm O_2 and 35.0 ppm N_2 in H_2, the chromatograms highlighted in figure 3 were obtained. The first interrupted peak represents the bulk gas (hydrogen), the second peak having a retention time at 8.5 min represents the oxygen and the last peak having a retention time of about 12.8 min represents the nitrogen peak. It can be observed the decreasing evolution of O_2 and N_2 peaks from the first injection to the last (from back to front). A significant difference between peaks is visible from chromatograms corresponding to the first three injections.

The results of these chromatograms are presented in table 1. As it can be seen, the values of the first 4 runs were high compared with those expected from the gas material certificate. A slightly decrease was observed further and the correct results were obtained after the last run.

Although the concentration of components resulted over the first runs exceeded significantly the values of the standard gases, these could be quantified using an option of interpretation software - Calibration range tolerance, allowing a range tolerance of 500%.

The evolution of the data shown by the chromatograms revealed that the pressure reducer was contaminated with atmospheric air before being connected to the sample cylinder, which led inevitably to the contamination of the sample. The regulator was completely clean after 7 injections.

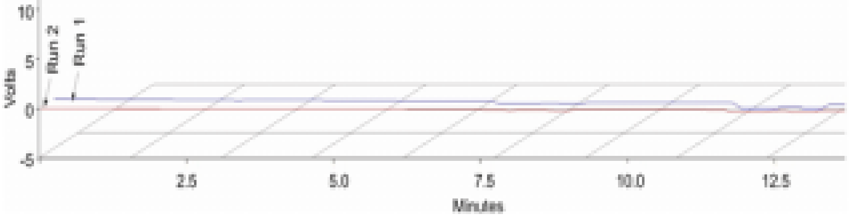


Fig. 1. The overlaid chromatograms of the purge gas (Helium 6.0) resulted on Molsieve 5A column over 2 runs

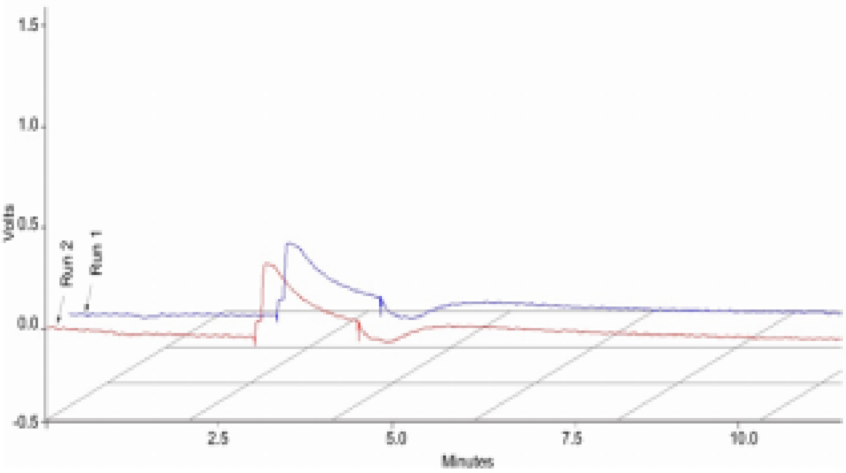


Fig. 2. The overlaid chromatograms of the purge gas (Helium 6.0) resulted on Q-Plot column over 2 runs

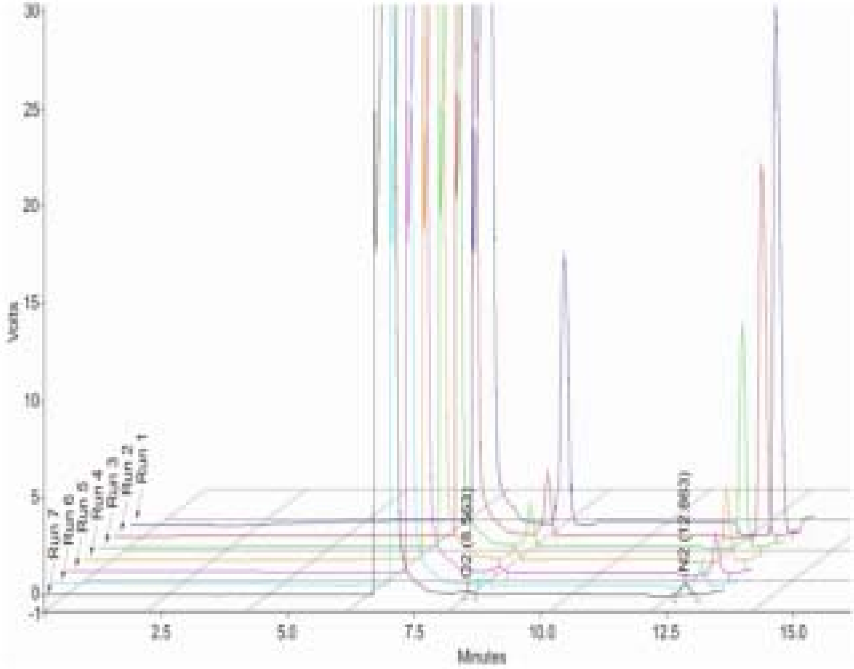


Fig. 3. The evolution of O_2 and N_2 peaks after the GC analysis of a sample with known composition (2.1 ppm O_2 and 35.0 ppm N_2 in H_2 balance), over 7 runs

Table 1

QUANTIFICATION OF O_2 AND N_2 IN A GAS MATERIAL WITH KNOWN COMPOSITION (2.1 ppm O_2 AND 35.0 ppm N_2 IN H_2 BALANCE) WITHOUT PURGED PRESSURE REDUCER

Component (ppm) **Run**	**O_2**	**N_2**
1	930.3	1530.5
2	172.5	1035.2
3	110.7	565.0
4	24.3	170.6
5	7.4	93.4
6	3.3	53.2
7	2.1	34.9
Certified value (ppm)	2.1	35.0

It must be mentioned that the sample flowed continuously through a 30 μL sample loop with 7 mL/min while the GC was running.

The solution to avoid this possible source of analytical error is that prior to each analysis to purge very well the cylinder regulator and the external sample path to the GC system.

The results obtained after the purge of pressure reducer with a sample flow of 350 mL/min for 15 min are presented in table 2.

In this case, as seen from the table 2, the correct values were achieved faster, after 2 injections and the repeatability was great over 7 runs. This results in a short time of analysis, lower consumption of carrier gas and a higher lifetime of separation columns.

Before reaching the results shown in table 2, several tests were performed in order to determine optimal flow to eliminate contaminants in regulator membrane, so that the sample consumption be as low as possible.

Another problem that may occur is the contamination of the sample with impurities remained in the membrane of the pressure reducer after previous analysis. Particularly, figure 4 presents the overlaid chromatograms obtained after the analysis of 1.3 ppm CO_2 in N_2. It can be observed that the CO_2 peaks decreased over all the runs.

Component (ppm) / Run	O_2	N_2
1	4	51
2	2.2	35.7
3	2.0	35.5
4	2.1	35.5
5	2.0	35.0
6	2.1	34.9
7	2.1	35.0
8	2.1	35.0
RSD* %, n=7	3.3	0.92
Certified value (ppm)	2.1	35.0

* RSD relative standard deviation for runs 2-8

Table 2
QUANTIFICATION OF O_2 AND N_2 IN A GAS MATERIAL WITH KNOWN COMPOSITION (2.1 ppm O_2 AND 35.0 ppm N_2 IN H_2 BALANCE) WITH PURGED PRESSURE REDUCER

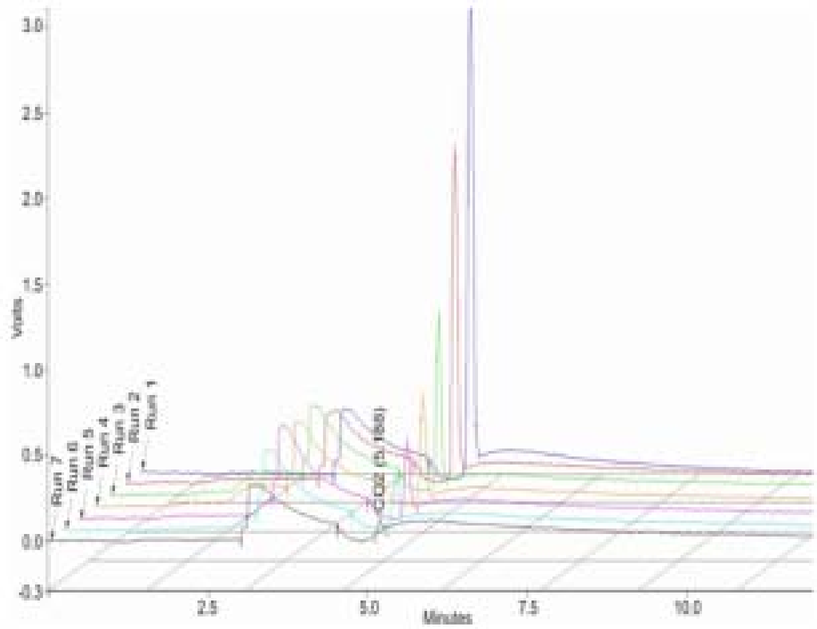


Fig. 4. The overlaid chromatograms of the sample to be analyzed with known composition (1.3 ppm CO_2 IN N_2 balance) obtained over 7 runs

Component (ppm) / Run	CO_2
1	63.5
2	43.0
3	22.1
4	13.7
5	8.9
6	5.7
7	1.3
Certified value (ppm)	1.3

Table 3
QUANTIFICATION OF CO_2 IN A GAS MATERIAL WITH KNOWN COMPOSITION (1.3 ppm CO_2 IN N_2 BALANCE) WITHOUT PURGED PRESSURE REDUCER

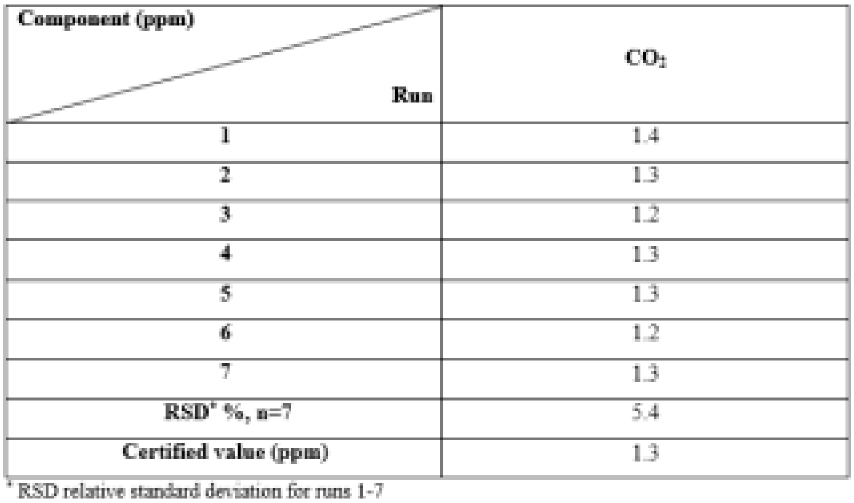
The concentration of CO_2 resulted after the interpretation of the chromatograms is reported in table 3. The first six values exceeded the certified value.

This can be explained by the fact that the same pressure reducer was used before, in the analysis of a Feromix sample (Ar + CO_2 18 %vol, ICIT- Ramnicu Valcea, Romania). A solution for this problem is first to purge the regulator with a pure inert gas (He or N_2) that is not required to be quantified as impurity in the next analysis and after that to purge with the sample.

The results obtained after the purge of pressure reducer are presented in table 4. The purge was performed in two steps, with 150 mL/min helium (5.0 grade) flow for 10 min and after that with 350 mL/min sample flow for 15 minutes. The repeatability was good over 7 runs.

Another option that may be considered, is directly purge with the sample, but this procedure could mean a significant loss of sample, because after several tests it has been proved more difficult to eliminate the carbon dioxide than nitrogen and oxygen contaminants. This phenomenon is due to physical processes governed by the relations between sizes of gas molecule and pores. For example, after the purge of pressure reducer with 350 mL/min sample flow rate for 15 min, the real results were obtained after 4 injections.

Table 4
QUANTIFICATION OF CO_2 IN A GAS MATERIAL WITH KNOWN COMPOSITION (1.3 ppm CO_2 IN N_2 BALANCE) WITH PURGED PRESSURE REDUCER



Component (ppm) / Run	CO_2
1	1.4
2	1.3
3	1.2
4	1.3
5	1.3
6	1.2
7	1.3
RSD* %, n=7	5.4
Certified value (ppm)	1.3

* RSD relative standard deviation for runs 1-7

Concluding, it is recommended to use different pressure reducers for each gas or to purge very well before the analysis, because in the membrane of the regulator, impurities may remain from the previous analysis.

Conclusions

The contamination is a critical issue that could influence the results of a gas analysis. This was demonstrated by the experiments involving several chromatographic measurements.

Two types of sample contamination with impurities from pressure reducer have been shown, namely with O_2 and N_2 from atmospheric air and CO_2 from the previous analysis. It has also been demonstrated that these problems could be avoided by purging the reducers. It was not enough that the sample flowed continuously through a 30 μL sample loop with 7 mL/min while the GC it was running.

Even if the purge involves both time and sample consumption, using this procedure a reproducible result can be obtained quickly, the carrier gas consumption is reduced and the lifetime of the separation columns is extended.

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References

1. RENSBURG, M. J., BOTHA, A., ROHWER, E., J. Chromatogr. A, **1167**, 2007, p. 102
2. LUONG, J., GRAS, R., CORTES, H.J., SHELLIE, R.A., J. Chromatogr. A, **1271**, 2013, p. 185
3. BAI, L., SMUTS, J., WALSH, P., FAN, H., HILDENBRAND, Z., WONG, D., WETZ, D., SCHUG, K. A., J. Chromatogr A, **1388**, 2015, p. 244
4. WURM, D.B., SUN, K., WINNIFORD, W.L., J. Chromatogr. Sci., **41**, 2003, p. 545
5. JI, Z., MAJORS, R.E., GUTHRIE, J.E., J. Chromatogr. A 842, 1999, p. 115
6. ZEEUW, J., NIJS, R.C.M., HENRICH, L.T., J. Chromatogr. Sci., 25, 1987, p.71
7. LECHNER-FISH, T.J., LUND, M.J., RYDER, S.L., Am. Lab., **24**, 1994, p. 288
8. BROWN, A.S., MILTON, M.J.T., COWPER, C.J., SQUIRE, G.D., BREMSER, W., BRANCH, R.W., J. Chromatogr. A **1040**, 2004, p. 215
9. PELLA, E., COLOMBO, B., Mikrochim. Acta, 1973, p. 697
10. SAFAVI, A., MALEKI, N., DOROODMAND, M.M., Anal. Chim. Acta **675**, 2010, p. 207
11. LAURENS, J.B., SWINLEY, J.N., CONING, J.P., J. Chromatogr. A, **873**, 2000, p. 229
12. WEIJUN, Y., J. Chromatogr. A, **1167**, 2007, p. 225
13. LAURENS, J.B., CONING, J.P., SWINLEY, J.N., J. Chromatogr. A, 911, 2001, p. 107
14. KIM, S.H., NAM, S.M., KOH, K. O., CHOI, Y.W., Bull. Korean Chem. Soc., **20**, no. 7, 1999, p. 843
15. WENTWORTH, W.E., VASNIN, S.V., STEARNS, S.D., MEYER, C., J. Chromatographia., **34**, 1992, p. 219
16. TIAN, X., YANG, W., YU, A., JIN, Q., Microchem. J., **52**, 1995, p. 139
17. MENDONCA, S., WENTWORTH, W.E., CHEN, E.C.M., STEARNS, S.D., J. Chromatogr., **749**, 1996, p. 131.
18. VASNIN, S.V., WENTWORTH, W.E., STEARNS, S.D., MEYER, C., J. Chromatographia., **34**, 1992, p. 226
19. JIN, Q., YANG, W., YU, A., TIAN, X., WANG, F., J. Chromatogr., **761**, 1997, p. 169
20. WENTWORTH, W.E., D’SA, E.D., CAI, H.; STEARNS, S., J. Chromatogr., **30**, 1992, p. 478
21. ROBERGE, M.T., FINELY, J.W., LUKASKI, H.C., BORGERDING, A.J., J. Chromatogr. A, **1027**, 2004, p. 19
22. POOLE, C.F., J. Chromatogr. A, 2015, http://dx.doi.org/10.1016/j.chroma.2015.02.061
23. FORSYTH, D.S., J. Chromatogr A, **1050**, 2004, p. 63
24. WENTWORTH, W.E., CAI, H., STEARNS, S., J. Chromatogr. A, **688**, 1994, 135
25. BROWN, A.S., VARGHA, G.M., DOWNEY, M.L., HART, N.J., FERRIER, G.G., HALL, K.I., NPL Report AS 64, Queen’s Printer and Controller of HMSO, Teddington, Middlesex, 2011, p. 10-15
26. HARTMANN, C.H., DIMICK, K.P., J. Gas Chromatogr., **4**, 1966, p.163
27. GUAN, Y., ZHANG, L., TANG, X., LU, P., J. Chromatographia, **23**, 1987, p. 566
28. SUNITHA, P., LAVANYA, K., KUMAR, A.A., KANTHAL L.K., KAUSIK, B., International Research Journal of Pharmacy, **3**, 2012, p. 11
29. CRACIUN, M.E., CRETU, G., MIRICIOIU, M., BIRLOIU, A.M., CLEJ, D.-D., NECHIFOR, A.C., Rev. Chim. (Bucharest), **65**, no. 6, 2014, p.621
30. NEAGU, M., PASCU, D.E., TRAISTARU, G.A., CRETU, G., NECHIFOR, A.C., BUNACIU, A.A., ABOUL-ENEIN, H.Y., Analytical Chemistry Letters, **3**(5-6), 2013, p. 314-321
31. CRETU, G., EFTIMIE TOTU, E., MIRON, A.R., NECHIFOR, A.C., Rom Biotech. Lett., **18**, 2013, p. 8271-8278
32. CRETU, G., MORLOCK, G., MIRON, A.R. NECHIFOR, A.C., Rom Biotech. Lett., **18**, 2013, p. 8657-8665
33. CRETU, G.C., MORLOCK, G.E., Food Chem., **146**, 2014, p. 104-112
34. CRETU, G.C., MORLOCK, G.E., NECHIFOR, G., UPB Sci. Bull., Series B: Chem. Mat. Sci., **75**, 2013, p. 69-78
35. NECHIFOR, A.C., PASCU (NEAGU), M., PASCU, D.E. TRAISTARU, G.A., Rev. Chim.(Bucharest), **64**, no. 3, 2013, p. 238

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