Using Hydrogen as a GC/MS Carrier Gas

Abstract

This document provides guidelines for the use of hydrogen carrier gas for the Chromatec GC/MS. The hydrogen generator “Crystal Ultra” with a Pressure Swing Adsorption (PSA) device is considered as a hydrogen source. The following are the safety precautions, modes and sensitivity. The analysis of pesticides is considered as an example.

Introduction

Helium is a fairly expensive gas. Moreover, in some regions of the world it is almost impossible to obtain. For this reason, it is becoming increasingly important to use cheaper and more readily available hydrogen as a carrier gas for GC/MS. Also, hydrogen has an advantage over helium in terms of chromatographic separation efficiency. The transition to hydrogen is not difficult for FID, ECD and other detectors. However, the increased reactivity of hydrogen imposes certain requirements and limitations when working with an MSD.

Safety precautions

Hydrogen is a flammable gas. If it accumulates indoors, inside the MSD, or inside the GC, it can cause a fire or explosion. Recommendations for the safe use of hydrogen are provided in the MSD User Manual.

GC/MS Chromatec is fully compatible with hydrogen carrier gas.

To alarm in case of hydrogen accumulation in the GC thermostat, SDO Chromatec produces a Hydrogen Leak Detector which can:

- signal a leak if the hydrogen concentration in the GC thermostat exceeds 4000 ppm.
- disconnect the GC from the hydrogen source if the hydrogen concentration in the GC thermostat has exceeded 10,000 ppm.

Selecting a hydrogen source

Basic requirements for hydrogen purity: hydrogen content > 99.999%, the minimum water and oxygen content is important. Despite the fact that one gas cylinder is cheaper than one hydrogen generator, continuous operation of the generator is cheaper and safer in whole.

Reasons for the higher safety of the generator:

- limited flow (300 ml/min), using a generator, unlike a cylinder, it is impossible to fill the room with hydrogen.
- low pressure (400 kPa) reduces explosion hazard.
- the stored amount of hydrogen is small (1 litre), in case of depressurization, only a small amount of hydrogen will get into the room, unlike a cylinder.

To provide GC-MS with hydrogen of proper quality, SDO Chromatec manufactures the “Crystal Ultra” hydrogen generator. The device is safe and the gas purity is sufficient enough to supply for the GC/MS. PSA as a part of the generator provides additional deep cleaning of gas and automatic regeneration of filters. Therefore, the hydrogen generator produces the gas of high quality and doesn’t require a service for a long period of time. The PSA also has a built-in device that automatically fills the generator with water. It also reduces operator involvement and is especially useful when equipment is running 24/7.

Specifications of the hydrogen generator "Crystal Ultra" with PSA

Hydrogen content	99.9995%
Oxygen content	0,2 ppm
Pressure	400 kPa
Hydrogen output	300 ml/min
Hydrogen volume	1 L
Water tank capacity	10 l
Operating time with one filling at maximum flow	72 h

Recommendations for connecting hydrogen

1. When working with hydrogen, the requirements for tube cleanness are higher than when working with helium, since hydrogen “flushes” impurities from the tubes more intensively as compared to helium.

2. When operating a “Crystal Ultra” hydrogen generator with PSA there is no need to use trap filters.

3. If the split flow of GC inlet exceeds 50 ml/min, it is recommended to guide it from the flow controller fitting outside the building or into the fume hood.

Recommendations when working with hydrogen

Hydrogen is not an inert gas. Therefore, in order to avoid unwanted chemical reactions in the GC inlet, it is recommended to:

• set the lowest possible inlet temperature;

• use the pulsed injection to reduce the presence time of the sample in the inlet;

• use a programmable inlet for cold sample injection;

• use liners with a taper at the bottom to minimize contact of the sample with the metal stop of the liner, use ultra-inert liners if possible;

• eliminate the use of dichloromethane and carbon disulphide as solvents to prevent the formation of acids in GC inlet at temperatures above 280 ° C;

• when carrying out a quantitative analysis, it should be considered that when switching from helium to hydrogen for some substances (for example, for polar compounds, nitroaromatics, phthalates):

  - the RSD may deteriorate;

  - the dependence of the signal intensity on the concentration can change from a linear to a quadratic.

Cleaning by hydrogen before starting

When the GC/MS is switched on with hydrogen for the first time a high background is present which gradually decreases. This process occurs both after launching a new device and after using helium. The background increase is caused by reaction of impurities with ions (protons) formed by electron ionization of hydrogen. Contaminations become volatile and are evacuated by a vacuum system. Thus, the ion source is purified using hydrogen. The presence of hydrogen in the ion source itself does not clean it because ionization is needed. Therefore, the cathode must be switched on for cleaning.

In the process of purification, the largest ions are with m/z 78, 91, 105 which belong to aromatic hydrocarbons.

To speed up the purification process reach the good vacuum, set the temperature of the ion source to 350 ° C in the "MS Tune" software, turn on scanning (in any range), turn off the dynode and the multiplier (uncheck the corresponding checkboxes) and leave it in this state from 2 to 12 hours. Also, to speed up the purification, you can increase the hydrogen flow through the column to 2-3 ml/min.

This procedure also helps to improve the shape of the peaks.

Analysis

Consider the operation of the GC/MS Chromatec with a hydrogen carrier gas using the example of pesticide analysis.

Sequence of steps

1. Connect hydrogen to chromatograph
2. Turn on the GC/MS.
3. Select the type of carrier gas “Hydrogen” in the Configuration of the Control Panel.
4. Transmit the method.
5. Wait until ready.
6. Clean the MSD ion source with hydrogen.

7. Perform a standard MS tune.

Equipment and materials

- Gas chromatograph Chromatec-Crystal 9000 with MSD
- Hydrogen generator "Crystal-Ultra" with PSA
- Column CR-5 ms (30 m × 0.25 mm × 0.25 µm), Cat. # 6.904.652
- Sample: a mixture of chlorine-, nitrogen- and phosphorus-containing pesticides, concentration 5 ppm

Instrument method

Chromatograph				
Analysis time			32,1 min	
Column				
Carrier gas flow			1 ml/min	
Column temperature				
	Isotherm 1:	50 °C	2 min	40 °C/min
	Isotherm 2:	140 °C	0 min	6 °C/min
	Isotherm 3:	250 °C	0 min	12 °C/min
	Isotherm 4:	280 °C	7 min	
Input port				
Temperature			275 °C	
Injection method			Splitless	
MSD				
Ion source temperature			250 °C	
Transfer line temperature			300 °C	
Solvent delay			4 min	
Emission current			20 µA	
Detector gain			100000	
Scan range			45-450 amu.	
Scan time			0,2 s	

Sample volume 1 µL. As with helium so and hydrogen column flow is set to 1 ml/min. Therefore, the linear velocity of helium is 36.1 cm/s, and that of hydrogen is 51.1 cm/s. As a result the analysis with hydrogen is shorter by 2 minutes.

Results and discussion

Examples of chromatograms are shown in Figures 1 and 2.

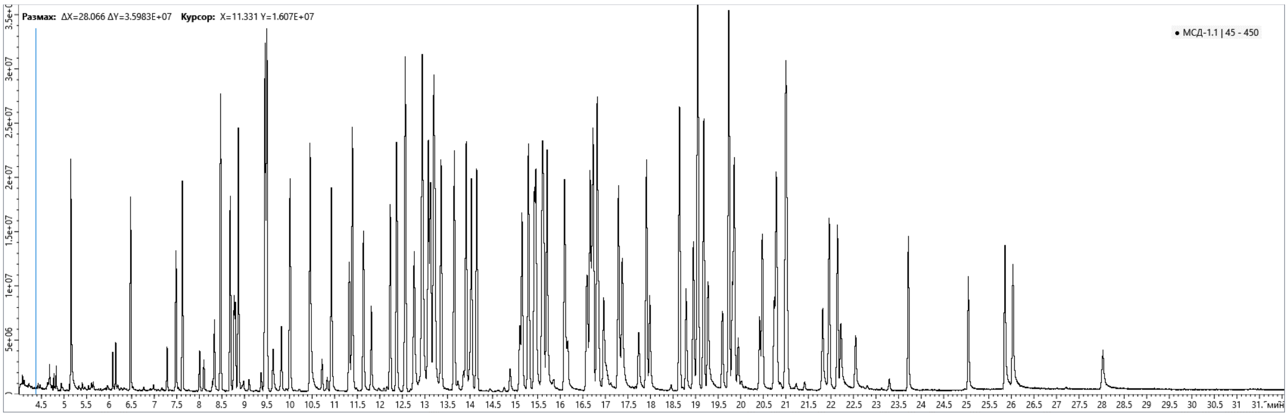


Figure 1. Helium carrier gas

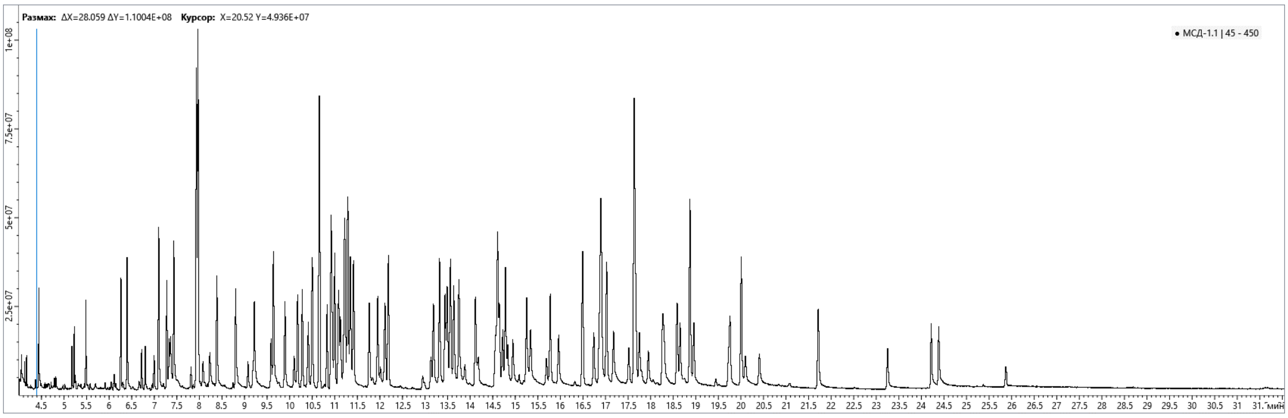


Figure 2. Hydrogen carrier gas

Due to the different velocity of the carrier gas, the order of some components has changed.

The separation quality and peak shape are good enough for both helium and hydrogen.

The intensity of the peaks with hydrogen is slightly higher, and the background is also higher.

Identification of components

Table 1 provides information on 78 pesticides in the sample to compare the Match and R.Match factors, characterizing the quality of identification.

Table 1

№	RT He, min	RT H_2, min	Component	He		H_2		He-H_2	
				Match	R.Match	Match	R.Match	Match	R.Match
1	5,16	4,44	Diisopropyl methylphosphonate	943	954	918	953	25	1
2	6,48	5,49	Dichlorvos	904	904	858	866	46	38
3	7,29	6,11	Oxydisulfoton	738	862	637	742	101	120
4	7,48	6,26	Hexachlorocyclopentadiene	885	887	711	742	174	145
5	7,63	6,4	Eptam	948	952	927	931	21	21
6	8,47	7,1	Diisocarb	936	937	926	927	10	10
7	8,69	7,28	Vernolate	938	938	924	926	14	12
8	8,77	7,34	Etridiazole	921	939	886	914	35	25
9	8,87	7,43	Pebulate	915	915	905	907	10	8
10	9,46	7,94	Chloroneb	929	939	929	945	0	-6
11	9,64	8,09	Tebuthiuron	922	943	891	894	31	49
12	10,01	8,39	Molinate	949	963	935	965	14	-2
13	10,46	8,81	Diethyltoluamide	933	934	897	908	36	26
14	10,93	9,22	Propachlor	933	935	838	846	95	89
15	11,32	9,59	Ethoprophos	886	886	873	887	13	-1
16	11,39	9,64	Cycloate	909	910	916	918	-7	-8
17	11,64	9,9	Chlorpropham	912	913	831	842	81	71
18	11,82	10,1	Trifluralin	885	885	762	763	123	122
19	12,23	10,42	Phorate	922	931	862	867	60	64
20	12,37	10,5	α-HCH	940	951	887	890	53	61
21	12,57	10,66	Hexachlorobenzene	958	959	926	927	32	32
22	12,93	11,09	Simazine	858	870	851	883	7	-13
23	12,77	11,13	Atraton	822	831	898	900	-76	-69
24	13,08	11,23	Atrazine	883	898	874	914	9	-16
25	13,13	11,22	β-HCH	903	903	756	814	147	89
26	13,2	11,35	Propazine	636	839	834	846	-198	-7
27	13,36	11,42	γ-HCH	945	949	827	836	118	113
28	13,65	11,77	Propyzamide	949	951	881	920	68	31
29	13,92	11,96	Tetrachloroisophthalonitrile	942	943	834	843	108	100
30	14,03	12,12	Disulfoton	809	838	670	716	139	122
31	14,15	12,19	δ-HCH	940	950	903	903	37	47
32	15,11	13,13	Metribuzin	867	871	866	871	1	0
33	15,16	13,19	Acetochlor	898	898	834	834	64	64
34	15,3	13,32	Vinclozoline	805	851	768	851	37	0
35	15,43	13,45	Alachlor	916	916	867	867	49	49
36	15,46	13,49	Simetryn	872	879	884	888	-12	-9

№	RT He, min	RT H_2, min	Component	He		H_2		He-H_2	
				Match	R.Match	Match	R.Match	Match	R.Match
37	15,61	13,56	Heptachlor	674	680	855	858	-181	-178
38	15,61	13,64	Ametryn	881	881	824	824	57	57
39	15,71	13,75	Prometryn	841	849	867	885	-26	-36
40	16,1	14,12	Terbutryn	916	920	919	923	-3	-3
41	16,17	14,19	Bromacil	874	876	896	898	-22	-22
42	16,6	14,56	Metolachlor	897	898	860	869	37	29
43	16,66	14,61	Chlorpyrifos	874	876	874	875	0	1
44	16,73	14,65	Aldrin	838	838	855	855	-17	-17
45	16,7	14,73	Cyanazine	818	819	851	854	-33	-35
46	16,82	14,79	DCPA	879	887	891	891	-12	-4
47	16,85	14,84	Parathion	857	858	827	840	30	18
48	16,97	14,95	Triadimefon	873	876	831	835	42	41
49	17,29	15,26	Diphenamid	929	929	909	921	20	8
50	17,38	15,34	MGK 264 Isomer 1	893	896	860	878	33	18
51	17,74	15,69	MGK 264 Isomer 2	875	878	863	865	12	13
52	17,91	15,78	Heptachlor epoxide	904	906	918	921	-14	-15
53	17,99	15,97	Clofenvinfos	855	868	839	896	16	-28
54	18,64	16,49	trans-Chlordane	925	925	788	802	137	123
55	18,8	16,74	Tetrachlorvinphos	874	877	782	782	92	95
56	18,95	16,92	Butachlor	846	846	804	810	42	36
57	19,05	16,9	cis-Chlordane	846	848	790	822	56	26
58	19,19	17,03	trans-Nonachlor	896	896	880	881	16	15
59	19,28	17,18	Napropamide	876	879	789	829	87	50
60	19,6	17,52	Profenofos	879	884	822	823	57	61
61	19,74	17,64	p,p'-DDE	936	945	880	949	56	-4
62	19,86	17,67	Dieldrin	833	833	849	850	-16	-17
63	19,95	17,95	Oxyfluorfen	832	853	787	788	45	65
64	20,42	18,29	Nitrofen	842	862	716	761	126	101
65	20,48	18,27	Endrin	915	922	698	698	217	224
66	20,79	18,59	Endosulfan	773	776	894	902	-121	-126
67	20,75	18,66	Chlorobenzilate	886	888	875	878	11	10
68	21	18,88	p,p'-DDD	781	846	895	897	-114	-51
69	21,03	18,96	Ethion	914	919	821	841	93	78
70	21,96	19,76	Endosulfan sulfate	925	925	886	892	39	33
71	22,15	20,01	p,p'-DDT	911	932	832	838	79	94
72	22,23	20,1	Hexazinone	903	911	853	863	50	48
73	22,55	20,41	Tebuconazole	907	916	872	889	35	27
74	23,72	21,72	Methoxychlor	884	889	863	866	21	23
75	25,05	23,25	Fenarimol	923	926	897	904	26	22
76	25,86	24,22	Permethrin	921	922	850	852	71	70
77	26,04	24,39	trans-Permethrin	917	918	854	859	63	59
78	28,03	25,88	Fluridone	926	939	905	923	21	16

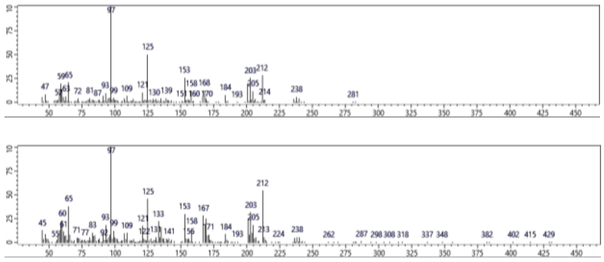
The identification quality is good enough for both helium and hydrogen. Match/R.Match values on helium are slightly higher, but in many cases this is due to insufficient separation of the components. For example, Nitrofen and Endrin are not separated with hydrogen, therefore, for both of these components the quality of identification has fallen sharply in comparison to helium. For the same reason, for some components with helium the quality of identification with helium is lower than with hydrogen. There are only a few cases (see next section) when Match/R.Match with hydrogen has dropped. It is caused by a change of the spectrum.

Out of the 78 components 48 have a Match/R.Match difference between helium and hydrogen less than 50. Another 17 have a Match/R.Match difference between helium and hydrogen from 50 to 100. But even in spite of such a difference, all components with hydrogen were identified correctly.

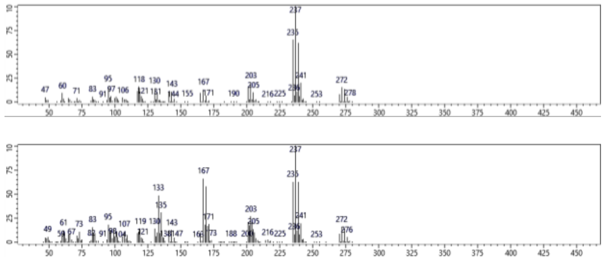
Examples of spectra with helium and hydrogen

Below there are examples of spectra with helium (upper) and hydrogen (lower) for substances most liable to change. In Table 1 these substances have a Match/R.Match difference for helium and hydrogen more than 100.

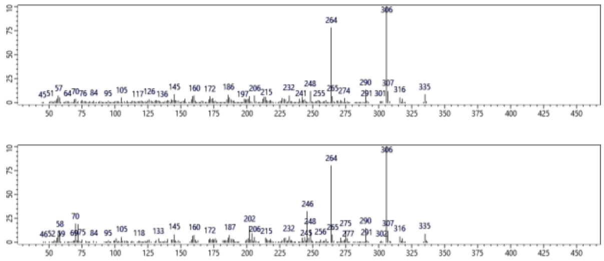
Oxydisulfoton



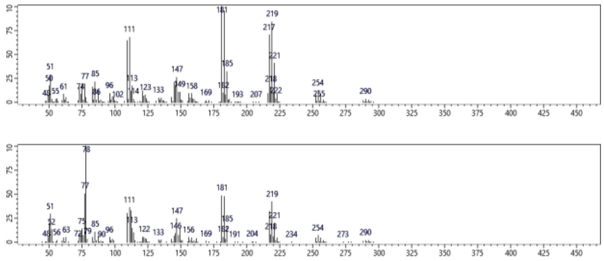
Hexachlorocyclopentadiene



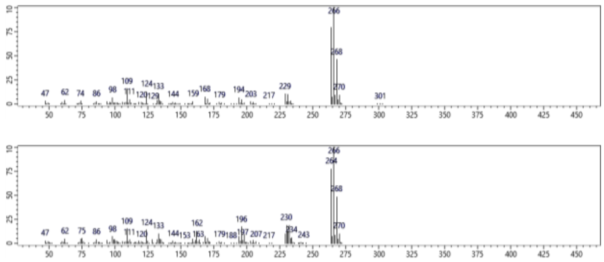
Trifluralin



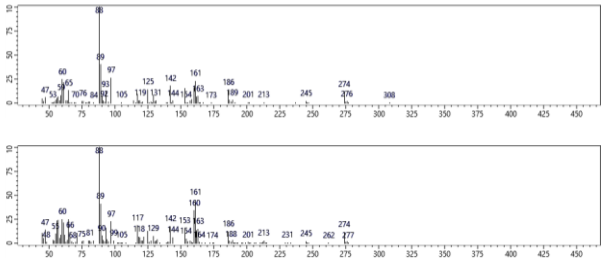
HCH (all isomers)



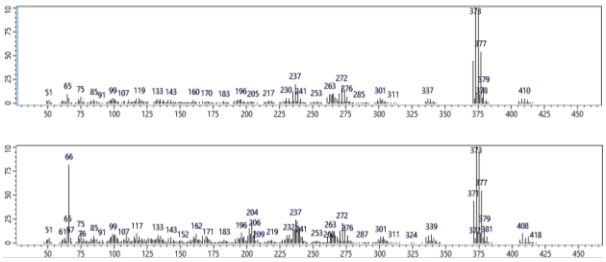
Tetrachloroisophthalonitrile



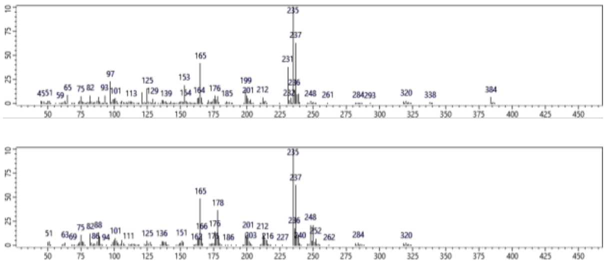
Disulfoton



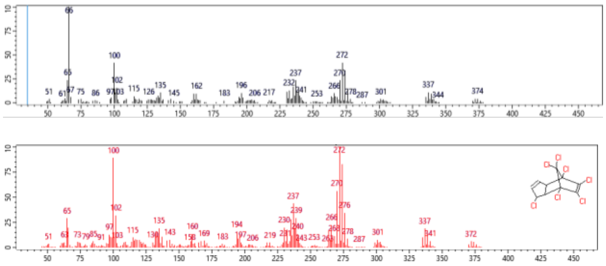
trans-Chlordane and cis-Chlordane



p, p '- DDD - the difference between Match/R.Match for helium and hydrogen is small although changes in the spectrum are present.



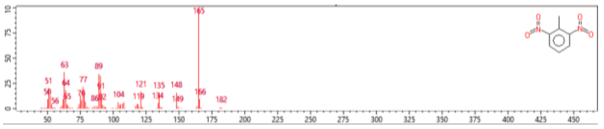
Heptachlor (instead of the spectrum for helium the library spectrum is shown since it is not well separated with helium)



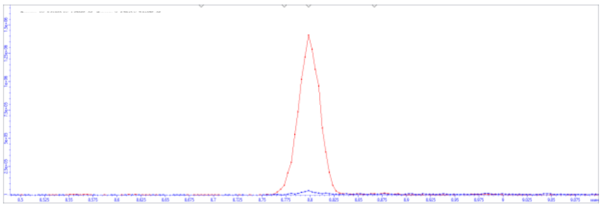
Due to the fact that the spectra of substances can change one should carefully consider the choice of quan and qual ions for quantitative analysis in the SIM mode. However in most of cases they remain the same as with helium.

Example of the reaction of the original substance

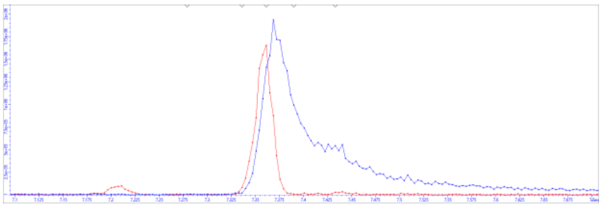
Reaction properties of hydrogen can be shown by 2,6-Dinitrotoluene. Its spectrum in the NIST20 library:



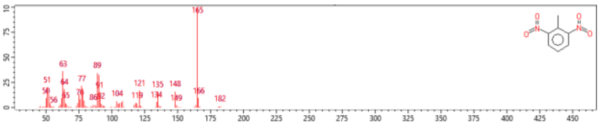
Its characteristic ion is m/z=165. When using a helium carrier gas there is a peak only at ionogram of m/z 165 (RT=8.8 min, red graph). There is no peak on the ionogram of m/z 122 (RT = 8.8 min, blue graph):



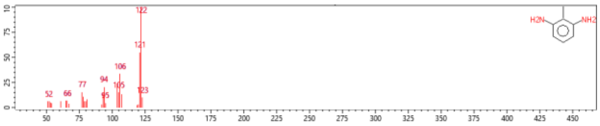
When using a hydrogen carrier gas, a peak of the same intensity appears on the ionogram of m/z 122 as on the ionogram of m/z 165 (RT=7.35 min, the graphs are given on the same scale):



The peak with a characteristic ion m/z=165 belongs to the original substance:



The peak with characteristic ion m/z=122 belongs to a new substance, 1,3-Benzenediamine, 2-methyl-:



It is a product of a reaction: nitro groups are converted to amino groups. Does this decrease the sensitivity for the original substance? S/N on helium is 2800 and on hydrogen is 700. This corresponds to the average decrease in sensitivity when switching from helium to hydrogen. Therefore, there is no significant decrease in sensitivity due to this reaction. The appearance of reaction products should be taken into account when working with nitrobenzenes.

Signal/Noise

Table 2 shows the Signal/Noise values for 30 components (10 at the beginning, in the middle and at the end of the analysis). When using helium, the S / N is 1.5-5 times higher. But for several components (for example, for Chloroneb, Fluridone) S/N is higher with hydrogen.

Table 2

№	Component	m/z	S/N He	S/N H_2	S/N (He) / S/N (H_2)
1	Diisopropyl methylphosphonate	123	10318	2440	4,2
2	Dichlorvos	109	8083	2958	2,7
3	Oxydisulfoton	125	536	126	4,3
4	Hexachlorocyclopentadiene	237	20297	5525	3,7
5	Eptam	128	5600	3172	1,8
6	Diisocarb	146	8326	2716	3,1
7	Vernolate	128	5949	3050	2,0
8	Etridiazole	211	5037	1398	3,6
9	Pebulate	128	5600	2818	2,0
10	Chloroneb	191	4368	5548	0,8
33	Acetochlor	223	2540	510	5,0
34	Vinclozoline	212	3763	924	4,1
35	Alachlor	188	6338	929	6,8
36	Simetryn	213	15115	4808	3,1
37	Heptachlor	272	9427	3699	2,5
38	Ametryn	227	10387	5917	1,8
39	Prometryn	241	11314	3603	3,1
40	Terbutryn	226	3169	1952	1,6
41	Bromacil	205	1640	815	2,0
42	Metolachlor	238	3279	822	4,0
69	Ethion	231	8049	1791	4,5
70	Endosulfan sulfate	272	5098	1118	4,6
71	p,p'-DDT	235	3755	2294	1,6
72	Hexazinone	171	3029	1173	2,6
73	Tebuconazole	250	589	518	1,1
74	Methoxychlor	227	11595	3793	3,1
75	Fenarimol	330	7709	1704	4,5
76	Permethrin	183	5660	2165	2,6

№	Component	m/z	S/N He	S/N H_2	S/N (He) / S/N (H_2)
77	trans-Permethrin	183	4630	1827	2,5
78	Fluridone	328	2223	2545	0,9

Conclusion

Hydrogen can be used as a carrier gas for the Chromatec GC/MS. Features of work with hydrogen:

1. Lower hydrogen price and availability compared to helium.
2. To reduce the cost of operation and improve safety, it is recommended to use a hydrogen generator "Crystal Ultra" with an PSA and a Hydrogen Leak Detector.
3. During operation, the ion source is cleaned and kept in a clean state. This reduces MSD maintenance and operating costs.
4. The separation efficiency with hydrogen is not worse than with helium, and the analysis time when using hydrogen can be significantly reduced due to the higher efficiency.
5. Slight changes in the spectrum of some substances are possible, but the quality of identification with hydrogen remains high enough when using traditional libraries of mass spectra.
6. The Signal/Noise value with hydrogen can be reduced by 1.5-5 times, depending on the analyzed compound.
7. Due to the reactivity of hydrogen, the formation of new substances and deterioration of the RSD are possible. Also the calibration dependence can change from linear to quadratic. As with helium, multi-point calibration is recommended for quantitative analysis.