GCMS helps to chemical disarmament

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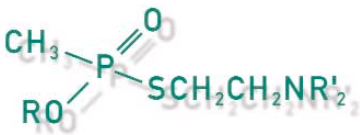
The V-type chemical warfare agent VX [O-ethyl S-diisopropylaminoethyl methylphosphonothioate] and its isomer, Russian VX [O-isobutyl S-(2-diethylamino) methylphosphonothioate] are highly toxic, persistent and included among the stockpiles of the United States and the former Soviet Union. The complete formula for V-type nerve agents is:



For the most „traditional" compounds of this series known since 1950, i.e.
(VX) R = Et, R' = iso-Pr
and for Russian
VX (RVX) R = iso-Bu, R' = Et.

The process proposed and used in Russia for destruc-tion of phosphorus-containing warfare agents includes chemical processing by mixtures of reagents containing potassium isobuty-late followed by treatment of the formed reaction mixture with bitumen. As a result, so-called bitumen-salt mixtures (BSM) are prepared.

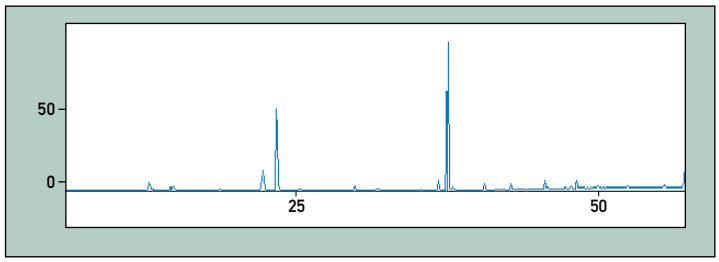


Figure 1: Typical chromatogram (total ion current) of the RVX-BSM extract by CH_2Cl_2

The goal of this work is GCMS identification of RVX decomposition products in RVX-BSM-mix-tures. Up to now, only limited information on the possible formation products has been available. Accessible literature relates to VX but not RVX destruction products.

Several dozens RVX-related compounds were detected in RVX-BSM mixtures (Figure 1). The most significant feature of RVX decomposition products is low information content of their EI mass spectra (Figure 2). The typical approach in these complex cases is not to use single analytical me-thods, but combinations including HPLC, LCMS, GC-FTIR, GC-AED, etc. However, there is an alternative way to restrict the test methods only to GCMS, while significantly improving interpretation of GCMS data by extra processing of GC retention indices (RI).

Determination and calculation of GC retention indices

For determination of GC retention indices (RI) the retention times of *n*-alkanes C_6-C_{20} and C_{21}-C_{26} have been determined in an artificial mix-ture and diesel fuel of common grade, respectively. The lin-log RIs have been calculated using simplest QBasic program. To predict the structures of unknown components the RI values published in [1] for another set of compounds relevant to RVX were recalculated. Reference RI values on standard non-polar polydimethyl siloxane stationary phases for evaluation of ΔRI increments have been taken from the private collection of one of the authors (I. Zenkevich).

Instrumentation

Mass Spectrometer: QP-5000
Gas Chromatograph: GC-17A

Results

26 components were identified in RVX-BSM by means of concurrent interpretation of MS and GC data. GCMS allows both characteristics to be obtained in the same run. Thanks to high repeatability of flow and temperature control the GC-17A ensures stable retention times for the components day after day, even after column reinstallation. So daily RT control was not necessary although RT values for the components were taken from different runs. Signals in mass spectra were also highly repeatable. The content of the „most suitable" sample and RIs of the components identified in the samples are listed in the table. Seven

Figure 3: Newly developed components increase the sensitivity of the LCMS-2010

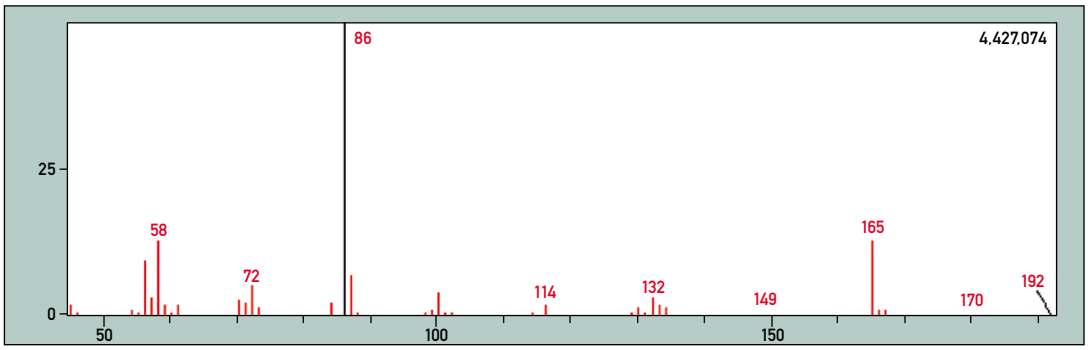


Figure 2: Mass spectrum of the principal component of RVX-BSM extract (# 18) as an example of its low information content for evaluating structure.

Nr.	Gehalt %	m/z base peak	RI	RI-Identifikationsdaten*	Endgültiger Strukturvorschlag
1	2	3	4	5	6
1	11,5	58	< 700	548 ± 8 (vgl.)	Diethylamin
2	0,2	60	847 ± 1	Approximierte RI-Ermittlung	CH_2 = CHSiBu
3	0,9	101	930 ± 1	895 ± 2 (vgl.)	Diethylformamid
4	2,9	86	976 ± 2	979 ± 2 (vgl.)	$Et_2NCH_2CH_2SH$
5	28,8	99	1034 ± 1	1002 ± 22 (vgl.)	N-Methylpyrrolidon**
M1	0,5	86	1076 ± 1	nach Methylierung gebildet	$Et_2NCH_2CH_2SMe$
S1	3,9	225	1142 ± 1	nach Silisierung gebildet	$MePO[OSi(Me)_3]_2$
6	0,2	86	1144 ± 2	auf einfachere Struktur reduziert	CH_2 = CH-S-$CH_2CH_2NEt_2$
S2	39,2	153	1214 ± 1	nach Silisierung gebildet	$CH_3PO(OiBu)OSi(Me)_3$
7	5,9	55	1266 ± 1	1255 ± 17 (vgl.)	Caprolactam**
8	45,8	86	1292 ± 2	1297 ± 18	$Et_2NCH_2CH_2$-S-iBu
9	5,9	97	1298 ± 1	1283 ± 10	$MePO(OiBu)_2$
10	0,1	113	1331 ± 1	1336 ± 10	$MePS(OiBu)_2$
11	0,1	86	1337 ± 1	1335 ± 4	$Et_2NCH_2CH_2$-S-Bu
M2	3,2	86	1424 ± 1	1446 ± 6	$MePO(OMe)SCH_2CH_2NEt_2$
12	0,9	86	1510 ± 1	1518 ± 8	$Et_2NCH_2CH_2$-S_2-iBu
13	0,5	86	1576 ± 1	1570	CH_2 = CH-S_3-$CH_2CH_2NEt_2$
14	0,5	86	1584 ± 1	1579 ± 28	$(Et_2NCH_2CH_2)_2S$
15	0,1	86	1689 ± 1	1675 ± 8	MePO(OiBu)-S-$CH_2CH_2NEt_2$
16	0,1	86	1740 ± 1	1736 ± 8	$Et_2NCH_2CH_2$-S_3-iBu
17	2,0	86	1782 ± 1	1768 ± 8	$MePO(SiBu)SCH_2CH_2NEt_2$
18	20,8	86	1818 ± 1	1823 ± 26	$(Et_2NCH_2CH_2)_2S_2$
19	0,3	86	2010 ± 1	2030 ± 28	$(Et_2NCH_2CH_2)_2S_3$
20	0,4	86	2021 ± 1	2018 ± 3	$Et_2N(CH_2CH_2S)_2CH_2CH_2NEt_2$
21	0,6	86	2128 ± 1	2140 ± 8	$MePO(OiBu)(SCH_2CH_2)_2NEt_2$
22	5,8	86	2648	2636 ± 8	$MePO(OiBu)(SCH_2CH_2)_3NEt_2$

Tabel 1: A Final identification of RVX decomposition products in RVX-BSM extracts *„ref." – The identification is based on the reference RI data; all other RI values are precalculated; ** Components of reaction mixture used for RVX destruction.

non-volatile compounds have been found as TMS (S1-S3) and methyl (M1-M4) derivatives. The total list of sample preparation procedures is presented in [2].

Resultant data from identification of RVX decomposition products in RVX-BSM extracts is sum-marised in the table.

Conclusion

Detailed interpre-tation of GC retention indices as GC-MS analytical parameters with the same importance as MS data, enables determination of reliable structures for 26 major products of Russian VX decomposition from 44 com-ponents found in RVX-BSM extracts, without the need for complex analytical methods. It is interesting to note that the ratio of identified/unidentified compounds is quite close to that of other contemporary works in this area. In spite of the application of chemical ionization mass spectra, the structures of 11 from 23 impurities in VX have been tentatively proposed [1], whilst application of modern LC-MS technique identifies two thirds of 38 VX decomposition products [3].

References

[1] D'Agostino P.A., Provost L.R., Visentini J., J. Chromatogr. 402 (1987) 221

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[3] D'Agostino P. A., Hancock J.R., Provost L.R., J. Chromatogr. A. 837 (1999) 93

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