Environmental Volatiles using a Headspace-GC/MSD Analyzer

Application Note

Environmental

Author

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Abstract

The Agilent Headspace Volatiles Analyzer, SP1 7890-0567, was used for the analysis of environmental volatiles in water. EC reporting requirements, as outlined in the 98/83/EC Directive, were met for all compounds. Calibration from 0.10 ppb–20 ppb and reproducibility at the lowest calibration level showed < 10% RSD. Peak shapes were very good for most compounds, and the early eluting gases were acceptable.

Introduction

Volatile organic compound (VOC) analyses is typically done by either purge and trap (P&T) or by headspace (HS), followed by GC/MS.

P&T is common to many USEPA methods and is also used outside the USA. It offers very good sensitivity as 5 or 25 mL of water are exhaustively extracted. The volatile analytes are concentrated on a packed trap, then backflushed into the GC. P&T can suffer from water carry over problems which can cause poor peak shape and reduced sensitivity. The hardware is more complicated than HS, there are a number of parameters to optimize and samples can foam.

Analysis by HS extraction is a more direct approach for volatiles in water. Compounds are forced into the headspace above a sample in a sealed vial. This is done primarily by heating and some analysts add salt to shift the equilibrium. The headspace is sampled and a portion delivered to the GC via a loop. HS extraction transfers less water to the GC, has fewer parameters to adjust and is simple to implement.

Headspace can achieve part-per-trillion levels using Selected Ion Monitoring (SIM). SIM is widely accepted for target compound analysis. The fast electronics in today's instruments allows for synchronous SIM/scan while maintaining sufficient data points for both modes. Target analytes can be quantified using the SIM data and all other compounds can be detected using the scan data.

This application note will detail the use of a HS-GC/MSD Analyzer for Environmental Volatiles in Water. Calibration, limit-of-quantitation, reproducibility and peak shape are addressed. Previous work Jacq etal. was used as a basis for this publication. [1]

Analyzer System Description

The system used is an Agilent Environmental Volatiles Analyzer, SP1 7890-0567. This is a factory preconfigured and pretested set of hardware and software. It consists of an Agilent 7697A Headspace Sampler, a 7890A Gas Chromatograph, and a 5975C Mass Selective Detector. The system is Retention Time Locked and a checkout sample is run before shipment to the enduser. A SIM acquisition table and calibration table, matched at 63 compounds, are derived from the 369 compound G1678AA Solvents+ Database\Library (DBL). Acquisition of SIM data for all 369 analytes is impractical and and not called for by any method. The SIM data can be used for quantitation and the scan data for deconvolution and detection of both target and non-target compounds. The Deconvolution Reporting Software and Solvents+ DRS DBL are included with the Analyzer. Laboratories can add/delete compounds from the SIM table and also look for all other compounds using DRS with the scan signal.

Experimental

The recommended instrument operating parameters are listed in Table 1. These are starting conditions and may have to be optimized.

Table1. Headspace, Gas Chromatograph and Mass Spectrometer Conditions

GC	Agilent Technologies 7890 A		
Inlet	EPC Split/Splitless or MMI		
Mode	Hot Split		
Heater	On 250 °C		
Pressure	On 8.4261 psi		
Total flow	On 27.162 mL/min		
Septum purge flow	On 3 mL/min		
Run time	23 min		
Gas saver	Off		
Split ratio	20:1		
Split flow	23.011 mL/min		
Cryo	Off		
S/SI Liner	Agilent 1.0 mm straight, no wool, p/n 392611999		
Oven	**120V or 240V**		
Oven ramp	°C/min	Next °C	Hold min
Initial		40	1.00
Ramp 1	10	250	1.00
Total run time	23 min		
Equilibration time	0.5 min		
Oven max temp	325 °C		
Alternate Oven Ramp			
	°C/min	Next °C	Hold min
Initial		32	0.40
Ramp 1	50	40	0.44
Ramp 2	10	250	1.00
Column	Agilent Technologies DB 5 MS UI, p/n 122-5533 UI		
Length	30.0 m		
Diameter	0.25 mm		
Film thickness	1.0 µm		
Mode	Constant pressure		
Pressure:	8.4261 psi		
Nominal initial flow	1.1506 mL/min		
Inlet	Front		
Outlet	MSD		
Outlet pressure	Vacuum		
RTL	System Retention Time locked to Toluene-d8 at 6.900 min		
Headspace	Agilent Technologies 7697A, 111 Vial Sampler		
Vial temp	85 °C		
Equilibration time	15 min		
Vial pressurization	10 psi		
Vial depressurization	4 psi		
Loop size	1.0 mL		
Loop temperature	85 °C		
Extraction time	0.3 min		
Mode	Single extraction		
Transfer line flow	> 20 mL/min		
Transfer line femp	120 °C		
Transfer line tubing	530 µm id Silcotek treated fused silica		
Vial size	20 mL p/n 5182-0837		
Vial cap	Aluminum, PTFE/Si, p/n 5183-4477		
MSD	Agilent Technologies 5975C, Triple-Axis Detector Trace Ion Detection enabled		
Drawout lens	3 mm Standard aperture drawout lens		
Solvent delay	0.0 min		
SIM groups	18		
SIM ions	4 to 18 ions/group		
SIM dwell	15–25 msec/ion		
Low mass	29 amu		
High mass	275 amu		
Threshold	5		
Sampling	1		
Quad temp	180 °C		
Source temp	300 °C		
Transfer line temp	250 °C		
Tune type	Autotune		
EMV mode	Gain Factor = 1		

Calibration and RTLocking Standards

RTLocking Mix – 20 compounds in n-propanol at 500 ppm each. Includes RTLocking compound Toluene-d8. Custom mix p/n 12377 available from Ultra Scientific, North Kingstown, RI. Diluted 10:1 in methanol then spiked at 10 µL into 10 mL water for each of the 6 RTLocking runs.

Calibration Mixes – 3 mixes each at 2000 ppm in methanol. These were codiluted into methanol at 20, 2, 0.2 0.5, 0.1 and 0.02 ppm. Methanol dilutions spiked at 10 µL into 10 mL water, resulting in 20, 2, 0.2 0.5, 0.1 and, 0.02 ppb concentrations for calibration. 54 volatile compounds p/n DWM-598N,6 gases p/n DWM-544 and 3 IS/SS compounds p/n STM-320N. Available from Ultra Scientific, North Kingstown, RI.

Split injection provides sufficient flow to flush the loop and transfer the analytes to the column in a short period of time. A split ratio of 20:1 allows sufficient sensitivity while minimizing the amount of water on the column. A lower split ratio, such as 10:1, gives better sensitivity with some loss in peak shape for the early eluting gases. Split ratios lower than 10:1 showed significant peak shape loss due to water on the column and lack of analyte refocussing at 40 °C.

The straight bore 1.0 mm liner without glass wool resulted in the best peak shapes at the 20:1 split. Both 2 mm and 4 mm liners with and without glass wool gave worse peak shapes for the earliest eluters. The transfer line, which feeds into the liner, had 35 mm protruding past the inlet septum. The liner is positioned upside-down to facilitate feeding of the fused silica into the liner. The column was 15 mm above the ferrule, which is more than the normal distance, and fed into the liner bottom.

The inlet top weldment was replaced with the accessory 7890A S/SL MMI Weldment for Headspace, p/n G3521A. This eliminates splicing the transfer line into the carrier line. The septum purge line exists but the carrier is fed directly from the inlet EPC module to the headspace sampler.

The oven program is that used by the RTL Solvents+ DBL, G1678AA. An initial oven temperature of 40 °C was chosen as many labs have difficulty achieving a lower value due to high ambient temperatures. An alternate oven program is shown for those labs that can use it. The lower initial temperature of 32 °C results in better peak shape for the early gases, which are acceptable at 40 °C. Remaining RTs are unchanged. If analyzing for only the 63 compounds reported here, the oven temperature can be reduced to 210 °C, shortening the run.

The 30 m × 0.25 mm × 1.0 µm DB 5MS UI column is that used by the RTL Solvents Database/Library G1678AA and was chosen for its upper temperature limit of 325 °C. Labs in the past have used DB-624 type columns with an upper temperature limit of 260–280 °C. DB-624 columns will give better peak shapes for the early eluters. The DB 5MS UI, however can remain in the oven with other columns used for semivolatiles analysis. A dual column configuration for volatiles and semivolatiles is offered in the Agilent 3-in-1 Environmental Analyzer, SP1 7890-0568.

The system was RTLocked to Toluene-d8 at 6.900 min. After clipping the column, a rerun and analysis of the locking standard is all that is needed to restore shifted peak times. Times for SIM groups, quantitation database entries and integration events do not have to be changed. RTLocking allows easier compound identification, especially with Deconvolution Reporting Software (DRS) and scan data. Additional RTL application notes detailing the numerous benefits of RTL are available at www.agilent.com/chem.

The headspace vial temperature was 85 °C, equilibrated for 15 min, providing the necessary sensitivity and calibration range. Vial pressurization of 10 psi is slightly higher than that created by the temperature alone, resulting in minimum dilution.

The standard 3 mm drawout lens was used for best sensitivity and sufficient linearity across the calibration range of 0.02–20 ppb.

The subset of compounds was taken from USEPA Method 524 and is typical of many EU methods. A quantitation database of 63 compounds was built from the 369 compound Solvents DBL. AutoSIM Setup was used to build the initial SIM acqusition table. This was modified to 2–3 ions/compound for optimum identification and cycle time.

Methanolic standards were co-diluted from three 2000 ppm commercially available standards. A 10 µL spike into 10 mL water was used to achieve the calibration levels. The highest methanol mixed standard at 20 ppm was stable for only a few days. All other levels had to be remade daily for reproducible performance of the early eluting gases.

The methanol standards were at 20, 2, 0.2 0.5, 0.1, and 0.02 ppm. The resulting concentrations in water were 20, 2, 0.2 0.5, 0.1, and 0.02 ppb.

IS/SS compounds were present, but only used for tracking performance. All calibrations were done external standard, ESTD, which will show worst case performance compared to ISTD. Either fluorobenzene or Toluene-d8 can be used for an ISTD.

The RTLocking Mix was not used for calibration. The 20 compound mix was used for a daily RTLocking check and for overall system performance.

Results

A total ion chromatogram (TIC) of the SIM ions is shown in Figure 1. The SIM groups are numbered and correspond to those in Table 2. All 63 drinking water analytes elute within 18 min.

The %RSD for the multi-level calibration is shown in Table 2. The reported %RSD is that for the response factors from 5 calibration levels, 0.10 ppb to 20 ppb. Of the 63 compounds, 61 show less than a 10% RSD. The remaining 2 compounds (**), dichloromethane and naphthalene, have 14% RSD. This is due to laboratory contamination, evident at the lowest calibration level of 0.1 ppb. A sixth calibration level of 0.02 ppb (20 ppt) was also run. The compounds marked with (*) still achieved a single digit %RSD of the response factors. The average %RSD for all 63 compounds is 3%, which is excellent.

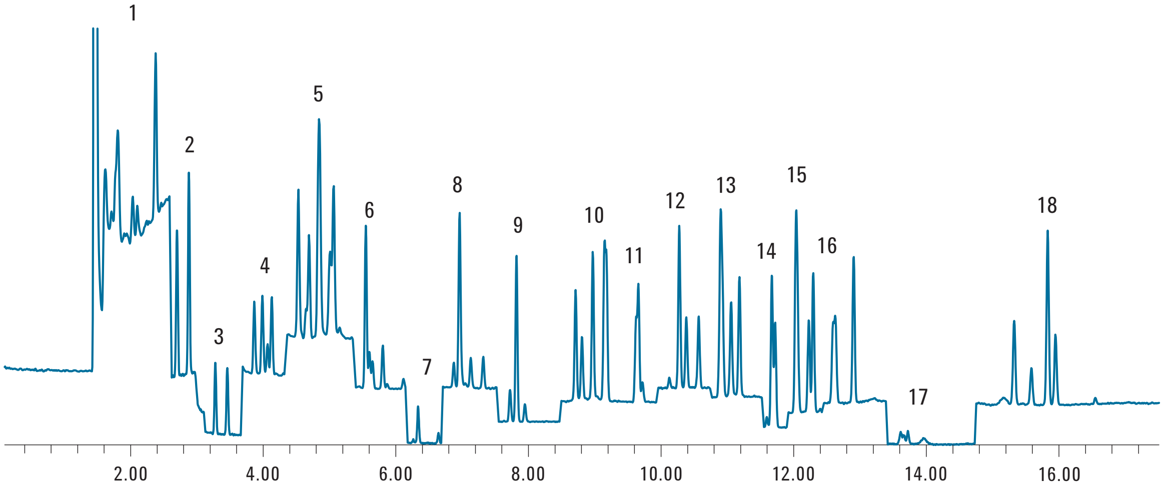


Figure 1. *200 ppt spike in lab water, SIM groups numbered.*

Table 2. *Calibration %RSD for SIM Analytes*

	Analyte	**R.T.**	**CAS no.**	**%RSD 20–0.1**		**Target**	**Q1**	**Q2**	**SIM Grp**
1	Dichlorodifluoromethane	1.687	75718	5		85	87	101	1
2	Chloromethane	1.784	74873	6		50	52		1
3	Vinyl Chloride	1.874	75014	8		62	64		1
4	Bromomethane	2.074	74839	6		94	96		1
5	Chloroethane	2.145	75003	7		64	66	49	1
6	Trichlorofluoromethane	2.404	75694	4		101	103	66	1
7	1,1-Dichloroethene	2.715	75354	6	*	61	96	98	2
8	Dichloromethane	2.884	75092	14	**	49	84	86	2
9	1,2-Dichloroethene (trans)	3.279	156605	4	*	96	98	63	3
10	1,1-Dichloroethane	3.456	75343	5		63	65	83	3
11	1,2-Dichloroethene (cis)	3.856	156592	6	*	61	96	98	4
12	2,2-Dichloropropane	3.985	594207	2		77	41	79	4
13	Bromochloromethane	4.064	74975	7	*	130	49	128	4
14	Chloroform	4.124	67663	2	*	83	85	47	4
15	1,1,1-Trichlorethane	4.528	71556	1	*	97	99	61	5
16	1,2-Dichloroethane	4.636	107062	1		62	64	63	5
17	1,1-Dichloropropene	4.679	563586	1	*	75	39	110	5
18	Benzene	4.828	71432	3	*	78	77	52	5
19	Carbon Tetrachloride	4.851	56235	2	*	117	119	121	5
20	Fluorobenzene (surr)	5.061	462066	2	*	96	70	50	5
21	Trichloroethene	5.545	79016	4	*	95	130	132	6
22	1,2-Dichloropropane	5.602	78875	2		63	62	41	6
23	Dibromomethane	5.650	74953	2	*	174	93	95	6
24	Bromodichloromethane	5.803	75274	4	*	83	85	47	6
25	cis-1,3-Dichloropropene	6.338	10061015	3	*	75	39	77	7

(Continued)

Table 2. Calibration %RSD for SIM Analytes

	Analyte	R.T.	CAS#	%RSD 20–0.1		Target	Q1	Q2	SIM Grp
26	trans-1,3-Dichloropropene	6.881	10061026	4	*	75	39	77	7
27	Toluene	6.971	108883	5		91	92	65	8
28	1,1,2-Trichloroethane	7.140	79005	2	*	97	83	99	8
29	1,3-Dichloropropane	7.330	142289	3	*	76	41	78	8
30	Dibromochloromethane	7.735	124481	3	*	127	129	131	9
31	Tetrachloroethene	7.833	127184	1	*	166	164	129	9
32	1,2-Dibromoethane	7.962	106934	5	*	107	109	79	9
33	Chlorobenzene	8.731	108907	3		112	77	114	10
34	1,1,1,2-Tetrachloroethane	8.827	630206	3		131	133	117	10
35	Ethylbenzene	8.992	100414	2		91	106	51	10
36	m-Xylene	9.186	108383	1		91	106	105	10
37	p-Xylene	9.186	106423	1		91	106	105	10
38	Styrene	9.650	100425	3		104	103	78	11
39	o-Xylene	9.685	95476	2	*	91	106	105	11
40	Bromoform	9.749	75252	2	*	173	171	175	11
41	1,1,2,2-Tetrachloroethane	10.158	79345	9	*	83	85	95	12
42	Isopropylbenzene (cumene)	10.308	98828	2	*	105	120	77	12
43	1,2,3-Trichloropropane	10.316	96184	2	*	75	77	110	12
44	4-Bromofluorobenzene (surr)	10.414	460004	2		95	174	176	12
45	Bromobenzene	10.601	108861	4		77	156	158	12
46	n-Propylbenzene	10.938	103651	2	*	120	92	65	13
47	2-Chlorotoluene	10.966	95498	1	*	126	89	63	13
48	4-Chlorotoluene	11.096	106434	3	*	91	126	125	13
49	1,3,5-Trimethylbenzene	11.224	108678	3	*	105	120	77	13
50	tert-Butylbenzene	11.717	98066	2	*	119	91	134	14
51	1,2,4-Trimethylbenzene	11.767	95636	3	*	105	120	77	14
52	sec-Butylbenzene	12.083	135988	1	*	105	134	91	15
53	1,3-Dichlorobenzene	12.107	541731	1	*	146	148	111	15
54	1,4-Dichlorobenzene	12.280	106467	2	*	146	148	111	15
55	p-Isopropyltoluene (p-Cymene)	12.350	99876	3	*	119	134	91	15
56	1,2-Dichlorobenzene-d4	12.648	2199691	1	*	150	152	115	16
57	1,2-Dichlorobenzene	12.687	95501	2	*	146	148	111	16
58	n-Butylbenzene	12.967	104518	3	*	91	92	134	16
59	1,2-Dibromo-3-chloropropane	13.734	96128	4		157	75	155	17
60	1,2,4-Trichlorobenzene	15.431	120821	4		180	182	145	18
61	Naphthalene	15.694	91203	10	**	128	127	129	18
62	Hexachlorobutadiene	15.956	87683	2	*	225	227	223	18
63	1,2,3-Trichlorobenzene	16.070	87616	4	*	180	182	145	18

* Compounds were successfully calibrated with a sixth level at 0.02 ppb and still maintained a %RSD of <10%

** These two compounds showed background blank response which affected the lowest calibration level

The reporting levels for EC compounds are shown in Figure 2, together with the gases. Some laboratories want a Limit of Quantitation (LOQ) of 3 times lower than the reporting limit. These LOQs are achieved as the lowest calibration point, 0.10 ppb is below the requested value. The trihalomethanes are not listed as their reporting levels are 100 ppb total and detection limits are not a problem.

		% RSD ESTD	**Cal Range ppb**	**EC Reg ppb**	**Want LOQ (1) ppb**	**# Cal levels**
1.629	Dichlorodifluoromethane	5	0.10–20	–	5	–
1.723	Chloromethane	6	0.10–20	–	–	5
1.815	Vinyl Chloride	8	0.10–20	0.5	0.15	5
2.022	Bromomethane	6	0.10–20	–	–	5
2.091	Chloroethane	7	0.10–20	–	–	5
2.356	Trichlorofluoromethane	4	0.10–20	–	–	5
4.643	1,2-Dichloroethane	1	0.10–20	3.0	0.9	5
4.828	Benzene	3	0.02–20	1.0	0.3	6
5.552	Trichloroethene	4	0.02–20	10.0	3.0	6
7.851	Tetrachloroethene	3	0.02–20	10.0	3.0	6

1. The LOQ is not an EC regulation but is a want of some laboratories. The calibration levels used easily meet this request.

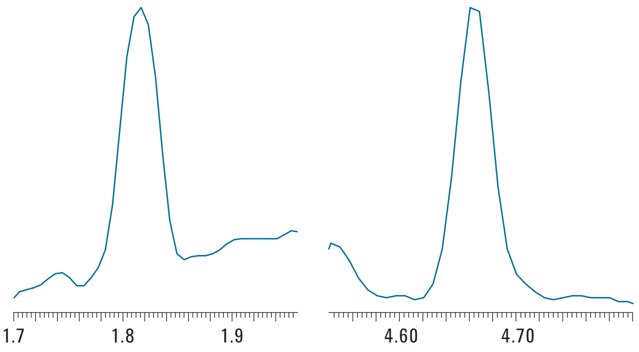
Figure 2. Linearity and calibration - EC named analytes and gases.

Reproducibility for the EC specified analytes is shown in Figure 3. Seven replicates of a 0.10 ppb standard were run. The %RSD of the raw areas is listed, with all below 10%. The average signal-to-noise (S/N) of the target ion is also shown, in the last column. These data demonstrate very good reproducibility of the system at the lowest calibration level.

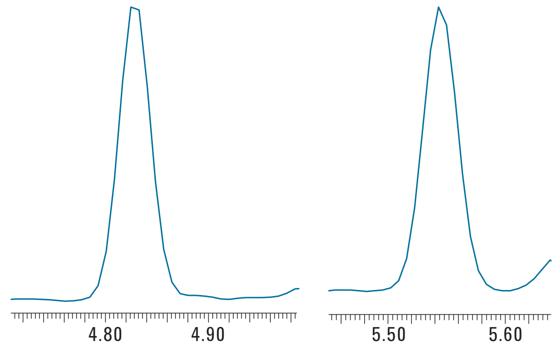
		n = 7 0.1 ppb %RSD	**0.1 ppb S/N**
1.629	Dichlorodifluoromethane	3	38
1.723	Chloromethane	8	19
1.815	Vinyl Chloride	4	9
2.022	Bromomethane	6	11
2.091	Chloroethane	8	6
2.356	Trichlorofluoromethane	4	76
4.643	1,2-Dichloroethane	5	25
4.828	Benzene	5	160
5.552	Trichloroethene	7	200
7.851	Tetrachloroethene	3	280

Figure 3. Reproducibility - EC specified analytes and gases.

Peak shape is important for integration, accurate quantitation and reproducibility. Shown in Figure 4. are target ion traces of four selected compounds. The earliest eluters can have peak shape problems due to their volatility and co-elution with water. In this system vinyl chloride, as an example, has acceptable peak shape even at the lowest calibration level.



Vinyl Chloride EIC 62 **1,2-Dichloroethane EIC 62**



Benzene EIC 78 **Trichloroethene EIC 95**

Figure 4. SIM quantitation Ions at 0.1 ppb for selected analytes.

The SIM TIC of a tap water sample is shown in Figure 5. The four trihalomethanes were quantitated and these are typical levels. None of the other 60 compounds were detected by SIM. This datafile was collected SIM/scan and the scan data processed through DRS. The DRS report showed no additional analytes detected from the 369 compound Solvents+ DBL.

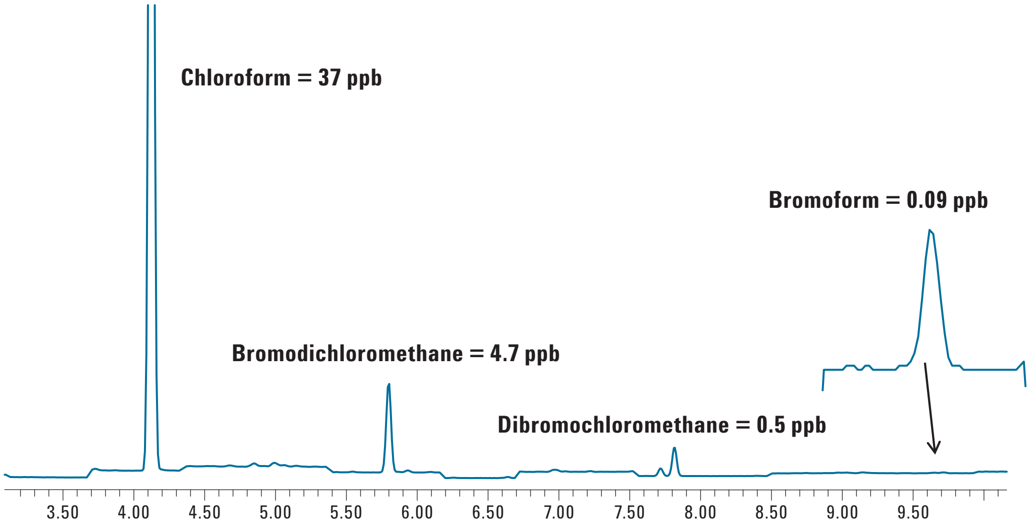


Figure 5. Agilent tap water sample, SIM TIC.

Conclusions

The Agilent Headspace Volatiles Analyzer, SP1 7890-0567, will meet the EC requirements for volatiles in water as outlined in the 98/83/EC Directive. Calibration from 0.10 ppb–20 ppb showed excellent %RSDs for all analytes. Reproducibilty at the lowest calibation level was < 10%. Peak shapes were very good for most compounds. Laboratories desire for LOQs at 3× lower than the required reporting limit were met.

References

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