Corrective Action Response
Formaldehyde

Date of Incident: Multiple. Identified March 3, 2022.

Date of Corrective Action: March 4, 2022 – April 14, 2022

Description of Corrective Action(s) Taken:

1. The current stock solution of Formaldehyde was run on the GC/MS to determine if the chemical still had the same chemical composition.
2. A new stock solution of Formaldehyde (C-22-0017) was ordered and, once received:
    a. Labeled appropriately, and
    b. Verified using the Volatile Chemical Method on GC/MS Instrument #1.
3. The chemical Formaldehyde, C-10-0007, was disposed of April 1, 2022.

Laboratory Number(s) (if applicable): N/A

Comment(s): This form was used in the interim while our Standard Operating Procedures (SOPs) are being revised. Under the proposed SOPs going forward, this would be considered an incident, and an incident form completed.

Date of Resolution: April 14, 2022

Seized Drugs — Applicable Analyst / Discipline — 04/14/22 — Date

Seized Drugs — Applicable Analyst / Discipline — 04/14/22 — Date

Lab Quality Manager — 14 April 2022 — Date

Laboratory Director — 14 April 2022 — Date

BRAZORIA COUNTY SHERIFF'S OFFICE
CRIME LABORATORY

Supplement to Corrective Action Plan – Formaldehyde

March 29, 2022

This supplement details the portion of the corrective action plan in which the expired chemical in question was characterized by instrumental analysis and any information on its viability discussed. The chemical in question, Formaldehyde (molecular formula CH_2O) was manufactured by Mallinckrodt – Lot 5016 KVSG circa 1998 with an expiration date of October 1998. According to the labeling information, the formulation of this chemical is formaldehyde – 37.2%, methanol – 12.4% and water with lesser ingredients such as heavy metals, sulfate, and chlorides.

Analysis of the chemical on the Gas Chromatograph/Mass Spectrometer (GC/MS) revealed the presence of methylal (dimethoxymethane) – molecular formula $C_3H_8O_2$. Research into the chemical determined that the pathway for formation is the reaction of formaldehyde with methanol. It is surmised that over the years, the formaldehyde reacted with the methanol in an acidic environment (acidic from the presence of the sulfates and chlorides in minor amounts) to eventually yield methylal. Essentially, two molecules of methanol reacting with one molecule of formaldehyde to yield methylal. With the expiration date being October 1998, there is no way of determining when the chemical converted entirely over to methylal from formaldehyde.

Formaldehyde is used as the secondary reagent in the two-part Marquis color test with the first reagent being concentrated sulfuric acid. Because the second step in the test requires formaldehyde, it can be inferred that because the chemical was in actuality methylal, the test results would be invalid. However, the reagents that comprise the Marquis color test – sulfuric acid and the expired formaldehyde have been tested each month as part of the Laboratory's ongoing quality program. Results of that testing with a known standard of methamphetamine has always yielded the correct color reaction. The question becomes – why does the quality test yield the correct results while one of the reagents used in the test is clearly not formaldehyde.

The answer to that question is that in the presence of an aqueous acid, methylal is hydrolyzed back to formaldehyde and methanol. Since addition of concentrated sulfuric acid is the first step of the Marquis color test, upon addition of the methylal – the second step – the methylal is hydrolyzed back to formaldehyde and thus the test proceeds to completion with the correct results. This outcome should be considered extremely fortunate for the Laboratory in that the Marquis test can be interpreted correctly; however, this is not the ideal mechanism. As detailed in the corrective action plan, a new lot of formaldehyde has been ordered and will be verified and placed into service.

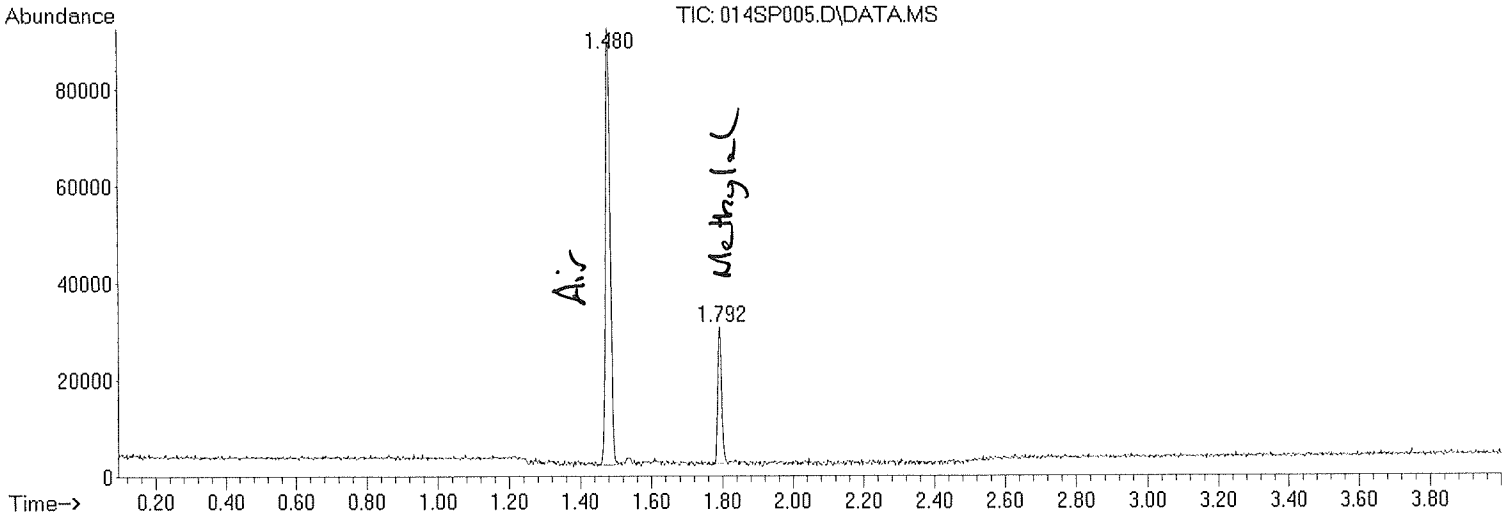
Included with this supplement is the chromatographic data from the instrumental analysis of the expired formaldehyde and information concerning the chemical properties of methylal. In summary, this supplement has addressed the chemical composition of the expired formaldehyde and why after being continually used in quality and casework testing – has allowed the Marquis color test to deliver the correct results.

Derek Sanders
Laboratory Director

DS
23 March 2022

Area Percent Report -- Sorted by Signal

Information from Data File:
File :D:\GCMS1DATA\STDS AND CHEMICAL VERIFICATION\032322\23MAR22A.
... 1A\23MAR22A.12P\014SP005.D
Operator : AGILENT GCMS #1
Acquired : 23 Mar 2022 2:35 pm using AcqMethod VOLATILES.M
Sample Name: FORMALDEHYDE STD 000001138
Misc Info : C-10-0007
Vial Number: 5



Retention Time	Area	Area %	Ratio %
Total Ion Chromatogram			
1.480	830725	79.191	100.000
1.792	218285	20.809	26.276

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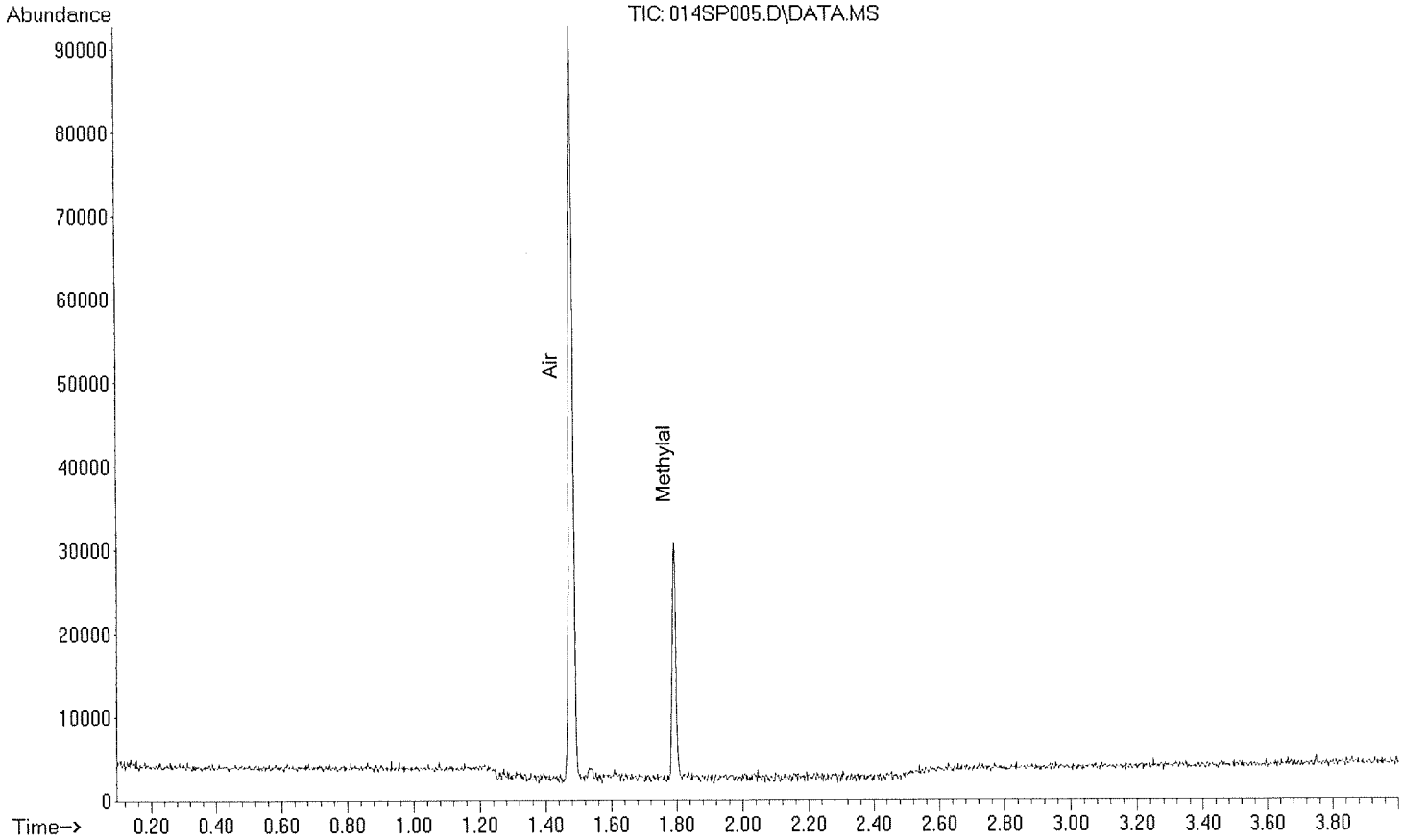
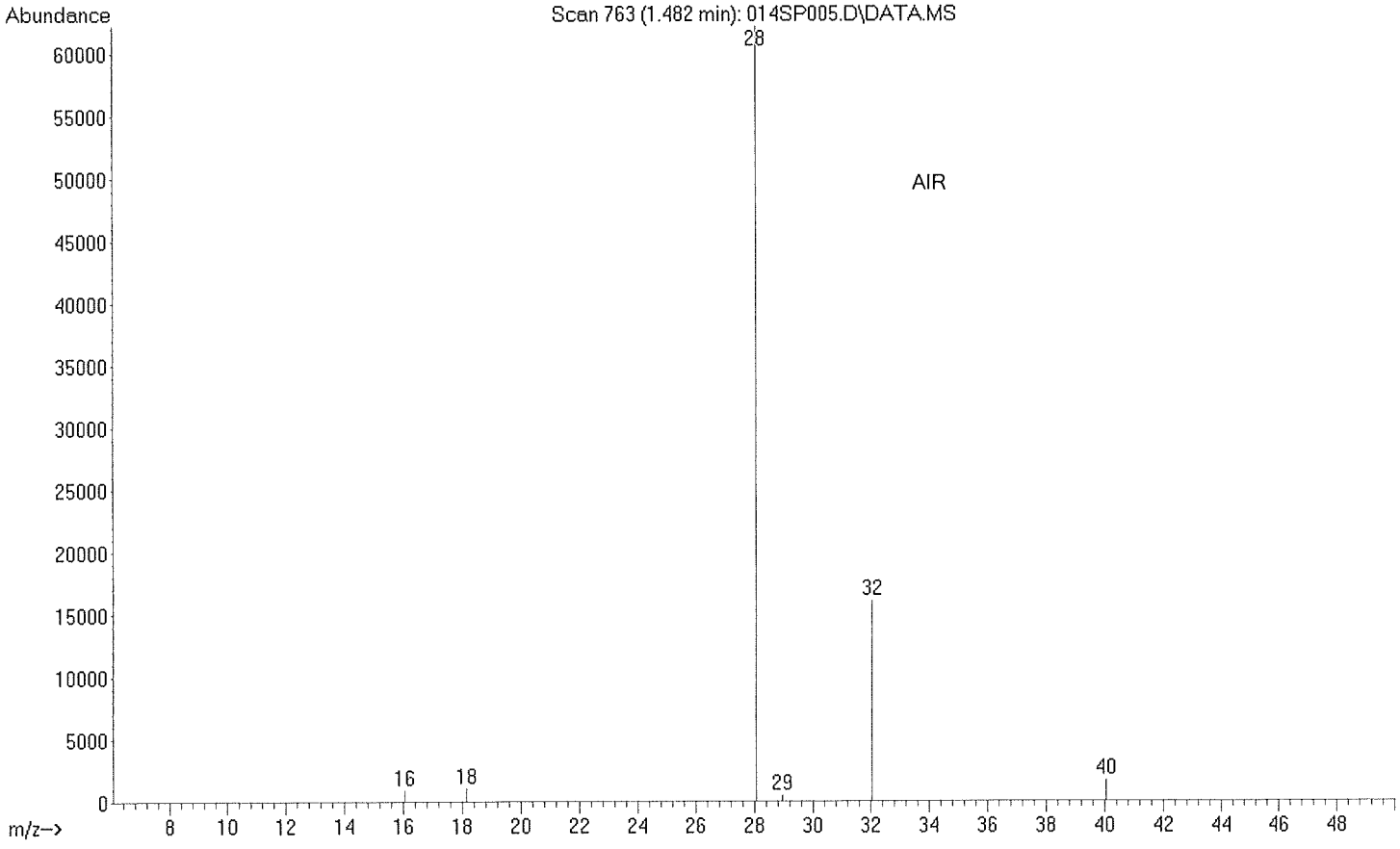
... 1A\23Mar22A.12p\014SP005.D
Operator : AGILENT GCMS #1
Instrument : Instrument #1
Acquired : 23 Mar 2022 2:35 pm using AcqMethod VOLATILE.M
Sample Name: FORMALDEHYDE STD 000001138
Misc Info : C-10-0007





DS
23 March 2022

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File        :D:\GCMS1Data\Stds and Chemical Verification\032322\23MAR22A.
...          1A\23Mar22A.12p\014SP005.D
Operator    : AGILENT GCMS #1
Instrument :    Instrument #1
Acquired    : 23 Mar 2022   2:35 pm using AcqMethod VOLATILE.M
Sample Name: FORMALDEHYDE STD                                  000001138
Misc Info   : C-10-0007
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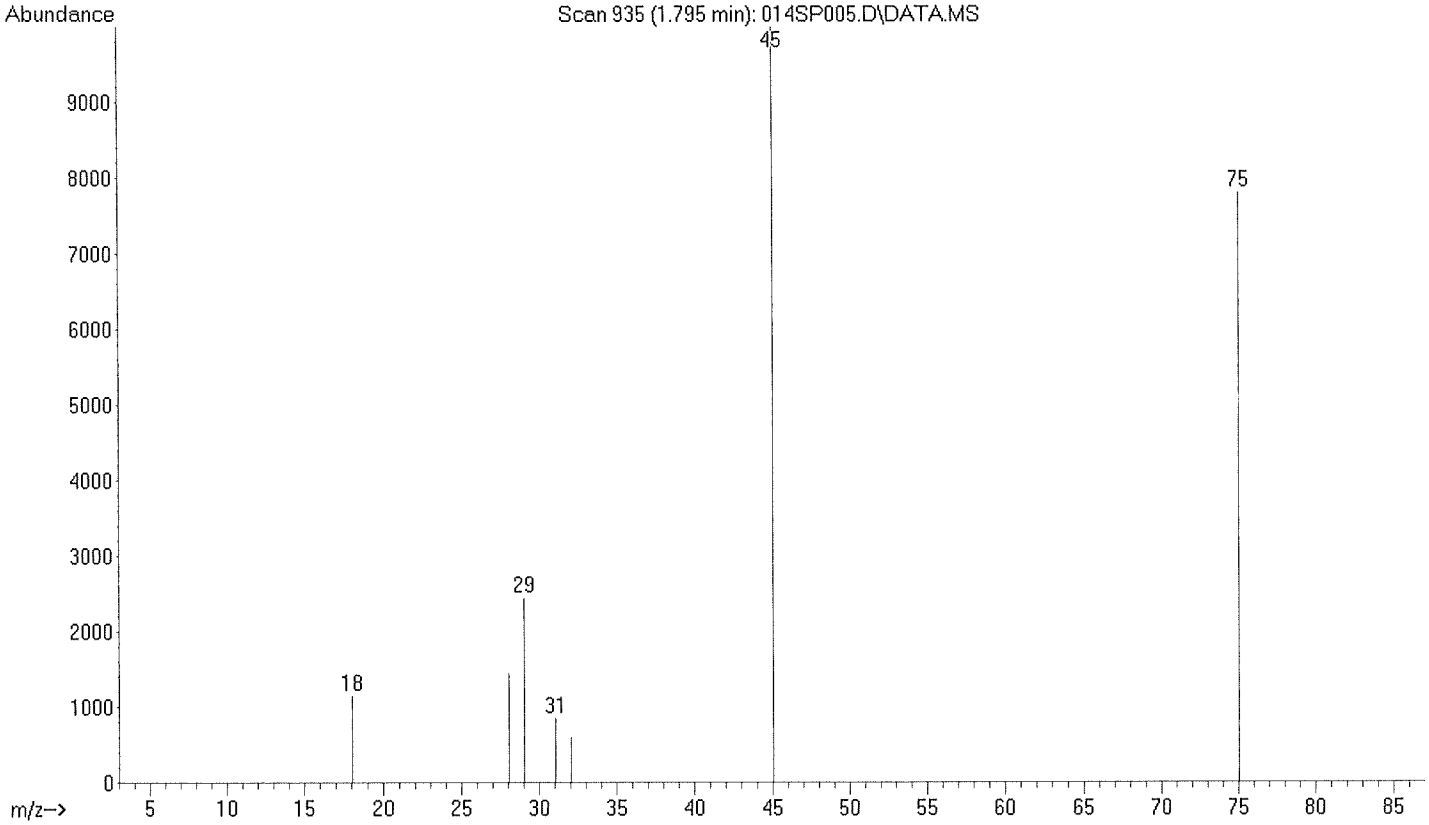

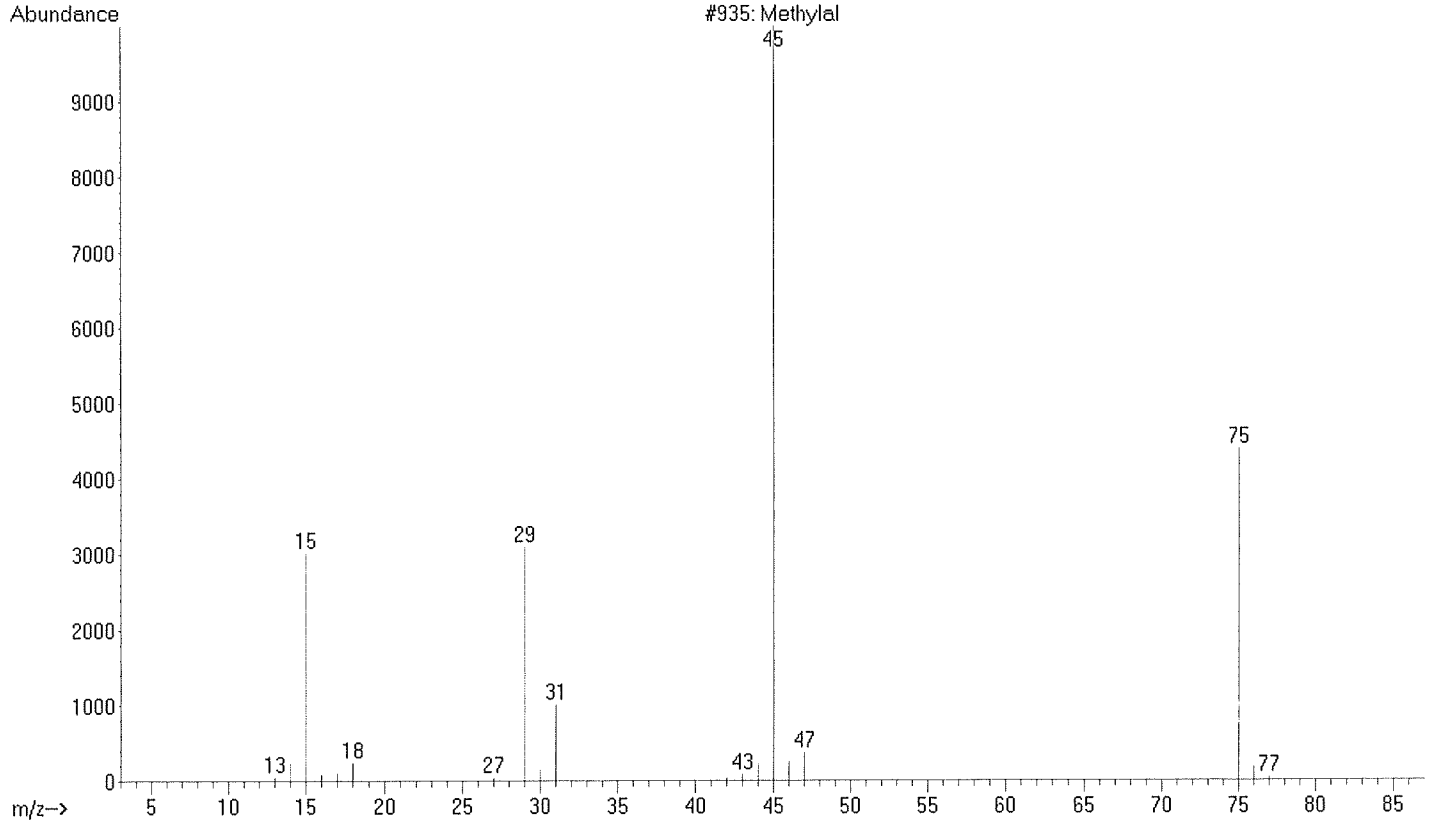

DS

23 March 22

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File        :D:\GCMS1Data\Stds and Chemical Verification\032322\23MAR22A.
...          1A\23Mar22A.12p\013BL001.D
Operator    : AGILENT GCMS #1
Instrument  :    Instrument #1
Acquired    : 23 Mar 2022   2:24 pm using AcqMethod VOLATILE.M
Sample Name: BLANK PRIOR TO FORMALDEHYDE STD C-10-0007      000001135
Misc Info   : AIR BLANK                                     000001135
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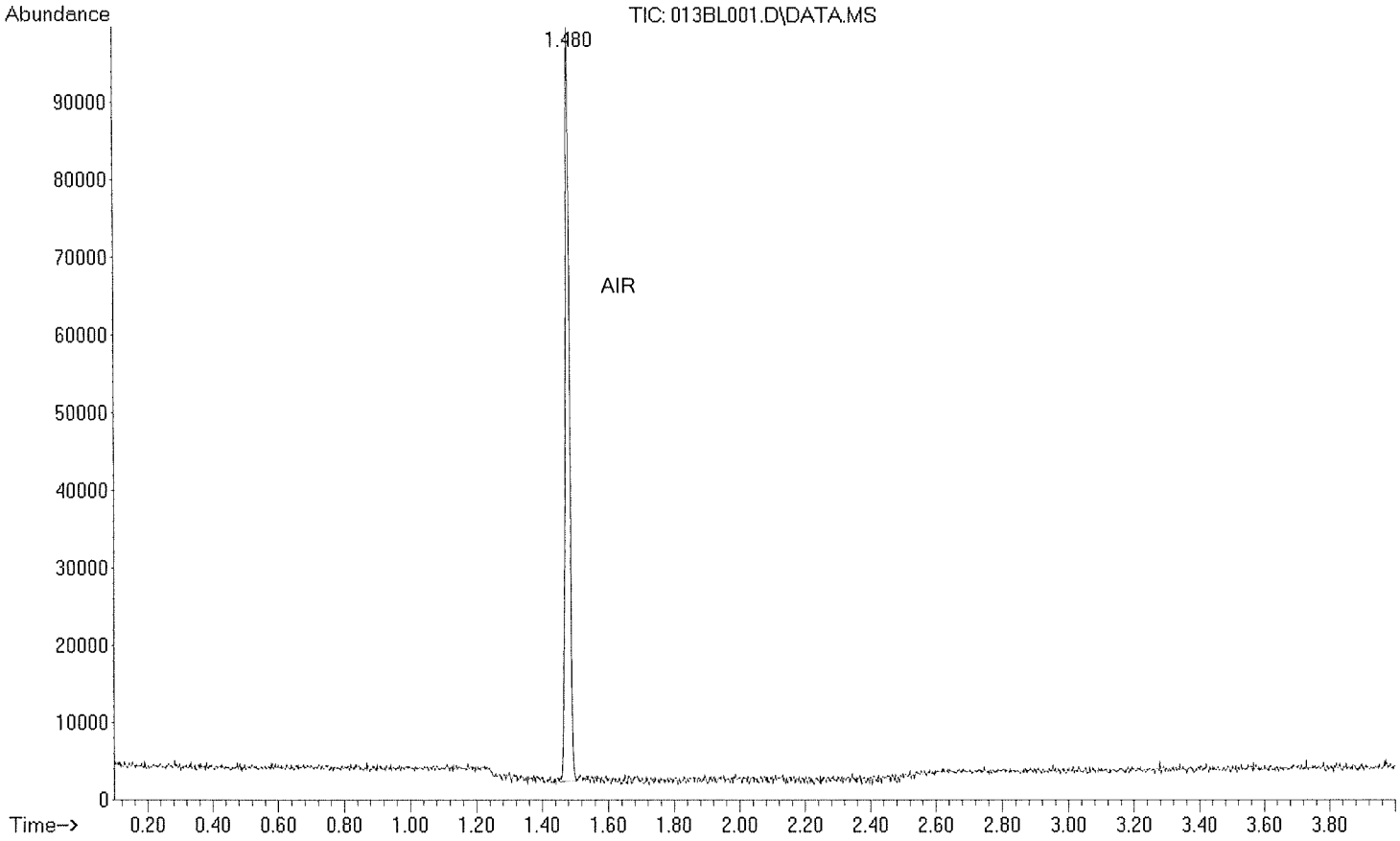
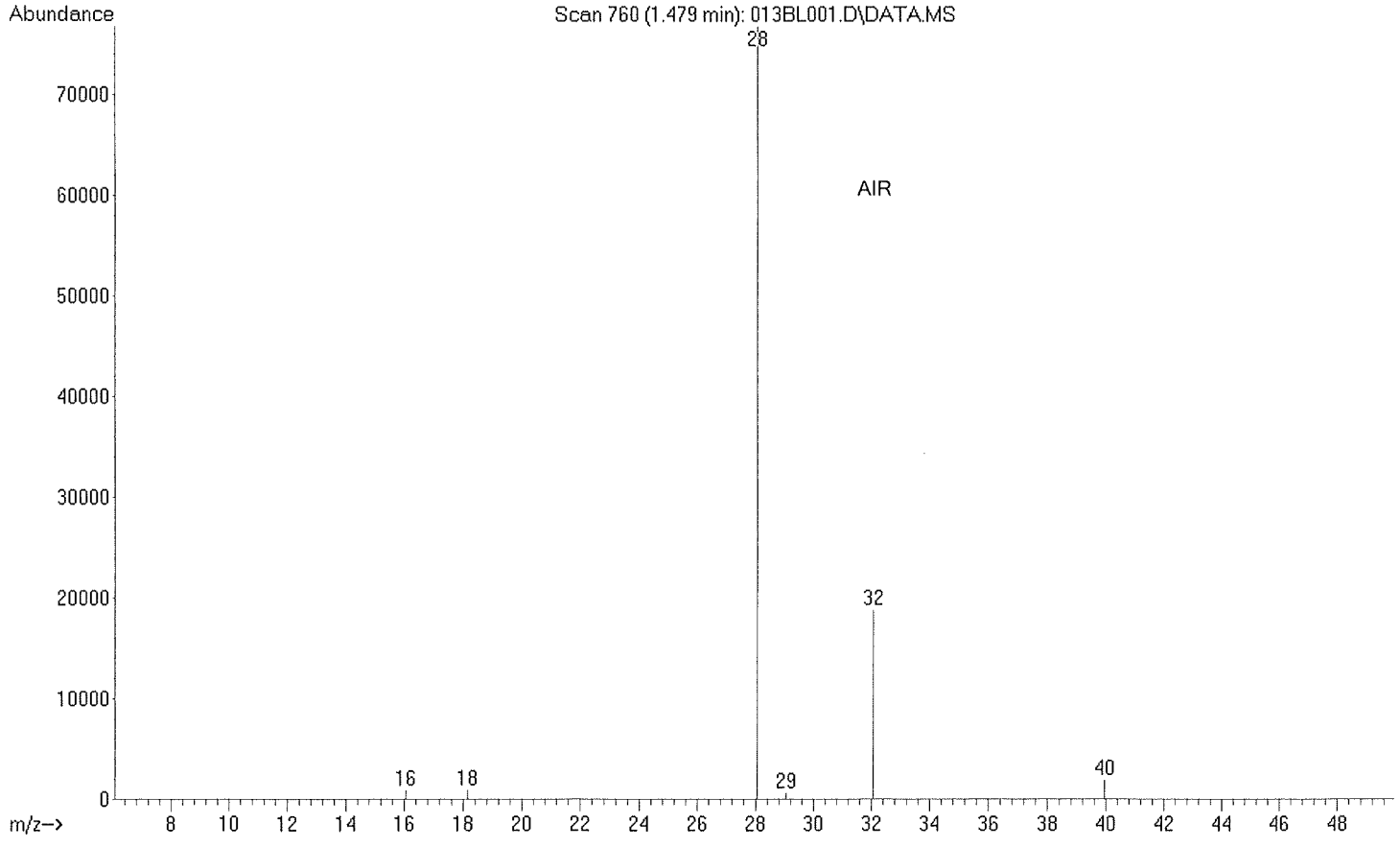




Dimethoxymethane

Dimethoxymethane, also called methylal, is a colorless flammable liquid with a low boiling point, low viscosity and excellent dissolving power. It has a chloroform-like odor and a pungent taste. It is the dimethyl acetal of formaldehyde. Dimethoxymethane is soluble in three parts water and miscible with most common organic solvents.

Contents

Synthesis and structure

It can be manufactured by oxidation of methanol or by the reaction of formaldehyde with methanol. In aqueous acid, it is hydrolyzed back to formaldehyde and methanol.

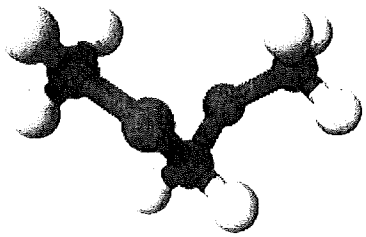
Due to the anomeric effect, dimethoxymethane has a preference toward the *gauche* conformation with respect to each of the C–O bonds, instead of the *anti* conformation. Since there are two C–O bonds, the most stable conformation is *gauche-gauche*, which is around 7 kcal/mol more stable than the *anti-anti* conformation, while the *gauche-anti* and *anti-gauche* are intermediate in energy.[5] Since it is one of the smallest molecules exhibiting this effect, which has great interest in carbohydrate chemistry, dimethoxymethane is often used for theoretical studies of the anomeric effect.

Applications

Industrially, it is primarily used as a solvent and in the manufacture of perfumes, resins, adhesives, paint strippers and protective coatings. Another application is as a gasoline-additive for increasing octane number. Dimethoxymethane can also be used for blending with diesel. [6]

Reagent in organic synthesis

Dimethoxymethane



Names	
Preferred IUPAC name	Dimethoxymethane
Other names	Formal Formaldehyde dimethyl ether Methylal Dimethylformal (DMFL) Formaldehyde dimethylacetal Methoxymethyl methyl ether Methylene dimethyl ether
Identifiers	
CAS Number	109-87-5 (https://commonchemistry.cas.org/detail?cas_rn=109-87-5) ✓
3D model (JSmol)	Interactive image (https://chemapps.stolaf.edu/jmol/jmol.php?model=COCOC)
Beilstein Reference	1697025
ChEBI	CHEBI:48341 (https://www.ebi.ac.uk/chebi/searchId.do?chebiId=48341) ✓

Another useful application of dimethoxymethane is to protect alcohols with a methoxymethyl (MOM) ether in organic synthesis.[7] This can be done using phosphorus pentoxide in dry dichloromethane or chloroform. This is a preferred method to using chloromethyl methyl ether (MOMCl). Alternatively, MOMCl can be prepared as a solution in a methyl ester solvent by reacting dimethoxymethane and an acyl chloride in the presence of a Lewis acid catalyst like zinc bromide:

$MeOCH_2OMe + RC(=O)Cl \rightarrow MeOCH_2Cl + RC(=O)(OMe))$.

The solution of the reagent can be used directly without purification, minimizing contact with the carcinogenic chloromethyl methyl ether. Unlike the classical procedure, which uses formaldehyde and hydrogen chloride as starting materials, the highly carcinogenic side product bis(chloromethyl) ether is not generated.[8]

References

1. *Merck Index*, 11th Edition, **5936**
2. NIOSH Pocket Guide to Chemical Hazards. "#0396" (https://www.cdc.gov/niosh/npg/npgd0396.html). National Institute for Occupational Safety and Health (NIOSH).
3. International Chemical Safety Card 1152 (https://www.ilo.org/dyn/icsc/showcard.display?p_lang=en&p_card_id=1152&p_version=2)
4. "Methylal" (https://www.cdc.gov/niosh/idlh/109875.html). *Immediately Dangerous to Life or Health Concentrations (IDLH)*. National Institute for Occupational Safety and Health (NIOSH).
5. Carey, Francis A.; Sundberg, Richard J. (2007). *Advanced organic chemistry* (5th ed.). New York: Springer. ISBN 9780387448978. OCLC 154040953 (https://www.worldcat.org/oclc/154040953).
6. Shrestha, Krishna P.; Eckart, Sven; Elbaz, Ayman M.; Giri, Binod R.; Fritsche, Chris; Seidel, Lars; Roberts, William L.; Krause, Hartmut; Mauss, Fabian (2020). "A comprehensive kinetic model for dimethyl ether and dimethoxymethane oxidation and NO interaction utilizing experimental laminar flame speed measurements at elevated pressure and temperature". *Combustion and Flame*. **218**: 57–74. doi:10.1016/j.combustflame.2020.04.016 (https://doi.org/10.1016%2Fj.combustflame.2020.04.016). hdl:10754/662921 (https://hdl.handle.net/10754%2F662921).

ChEMBL	ChEMBL15537 (https://www.ebi.ac.uk/chembldb/index.php/compound/inspect/ChEMBL15537) ✓
ChemSpider	13837190 (https://www.chemspider.com/Chemical-Structure.13837190.html) ✓
ECHA InfoCard	100.003.378 (https://echa.europa.eu/substance-information/-/substanceinfo/100.003.378)
EC Number	203-714-2
Gmelin Reference	100776
MeSH	Dimethoxymethane (https://www.nlm.nih.gov/cgi/mesh/2014/MB_cgi?mode=&term=Dimethoxymethane)
PubChem CID	8020 (https://pubchem.ncbi.nlm.nih.gov/compound/8020)
RTECS number	PA8750000
UNII	7H1M4G2NUE (https://fdasis.nlm.nih.gov/srs/srsdirect.jsp?regno=7H1M4G2NUE) ✓
UN number	1234
CompTox Dashboard (EPA)	DTXSID1025564 (https://comptox.epa.gov/dashboard/chemical/details/DTXSID1025564)
InChI	
InChI=1S/C3H8O2/c1-4-3-5-2/h3H2,1-2H3 ✓	

7. Martin Berliner and Katherine Belecki. "Synthesis of Alpha-Halo Ethers from Symmetric Acetals and in situ Methoxymethylation of an Alcohol" (http://www.orgsyn.org/demo.aspx?prep=CV11P0934). *Organic Syntheses*. **84**: 102.; *Collective Volume*, vol. 11, p. 934
8. "SYNTHESIS OF ALPHA-HALO ETHERS FROM SYMMETRIC ACETALS AND in situ METHOXYMETHYLATION OF AN ALCOHOL" (http://orgsyn.org/demo.aspx?prep=v84p0102). *orgsyn.org*. Retrieved 2018-09-13.

External links

- NIOSH Pocket Guide to Chemical Hazards. "#0396" (https://www.cdc.gov/niosh/npg/npgd0396.html). National Institute for Occupational Safety and Health (NIOSH).

Key: NKDDWNXOKDWJAK-UHFFFAOYSA-N ✓	
InChI=1/C3H8O2/c1-4-3-5-2/h3H2,1-2H3 Key: NKDDWNXOKDWJAK-UHFFFAOYAE	
SMILES	
COCOC	
Properties	
Chemical formula	$C_3H_8O_2$
Molar mass	76.095 g·mol^{-1}
Appearance	Colorless liquid[1]
Odor	Chloroform-like[1]
Density	0.8593 g cm^{-3} (at 20 °C)[1]
Melting point	−105 °C (−157 °F; 168 K)[1][3]
Boiling point	42 °C (108 °F; 315 K)[1][3]
Solubility in water	33% (20 °C)[2]
Vapor pressure	330 mmHg (20 °C)[2]
Magnetic susceptibility (χ)	−47.3·10^{-6} cm^3/mol
Hazards	
GHS labelling:	
Pictograms	
Signal word	**Danger**
Hazard statements	H225, H315, H319, H335
Precautionary statements	P210, P233, P240, P241, P242, P243, P261, P264, P271, P280, P302+P352, P303+P361+P353, P304+P340, P305+P351+P338, P312, P321, P332+P313, P337+P313, P362, P370+P378, P403+P233,

	P403+P235, P405, P501
Flash point	−18 °C (0 °F; 255 K)
Explosive limits	2.2–13.8%[2]
Lethal dose or concentration (LD, LC):	
LD_{50} (median dose)	5708 mg/kg (rabbit, oral)[4]
LC_{50} (median concentration)	18000 ppm (mouse, 7 hr) 15000 ppm (rat) 18354 ppm (mouse, 7 hr)[4]
NIOSH (US health exposure limits):	
PEL (Permissible)	TWA 1000 ppm ($3100\ mg/m^3$)[2]
REL (Recommended)	TWA 1000 ppm ($3100\ mg/m^3$)[2]
IDLH (Immediate danger)	2200 ppm[2]
Related compounds	
Related Ethers	Dimethoxyethane
Except where otherwise noted, data are given for materials in their standard state (at 25 °C [77 °F], 100 kPa).	
✗ verify (what is ✓✗ ?)	
Infobox references	

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