Analytical and Bioanalytical Chemistry (2023) 415:5–6
https://doi.org/10.1007/s00216-022-04429-1

ANALYTICAL CHALLENGE

Solution to arsenic speciation challenge

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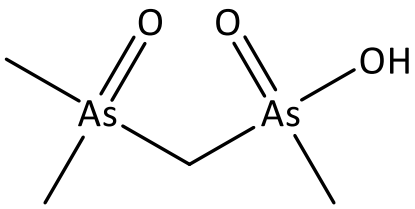
Accepted: 11 November 2022 / Published online: 4 January 2023

The winner of the arsenic speciation challenge (published in volume 414 issue 16) is:

Kevin Colizza, GSK Collegeville, PA 19426, USA.

The award entitles the winner to select a Springer book of their choice up to a value of €100,-.

Our Congratulations!



(dimethylarsonyl)dimethylarsinic acid

The presence of a (+)-ESI ion at *m/z* 258.9291 and a (−)-ESI ion at *m/z* 256.9146 indicates that these ions correspond to $[M+H]^+$ and $[M-H]^-$, respectively. The arsenic-containing molecular formula that best matches these two values is $C_4H_{12}As_2O_3$. There is a known arsenic-containing compound with this formula: dimethylarsinic acid anhydride, $(CH_3)_2As(=O)–O–As(=O)(CH_3)_2$. However, the lack of acidic hydrogen atoms in this molecule suggests that it may not yield the $[M-H]^-$ ion observed by (−)-ESI–MS. Furthermore, this known compound would not be expected to yield some of the fragment ions provided in the challenge [1], particularly *m/z* 164.8661 corresponding to $CH_3As_2^+$.

Table 1 summarizes chemical formula assignments for select ions, with rows grouped by common product ions and/or neutral losses. Elimination of dimethylarsinic acid anhydride is further supported by the presence of a trithiolated derivative, which indicates the presence of three oxygen atoms accessible to thiolation with H_2S. The combination of this information with the fragment assignments from Table 1 leads to the structure above. For additional details on the fragment and structure assignments, see the recent publication by Raab and coworkers [2].

It is not trivial to assign the systematic IUPAC name to this substance. One way to name this substance is to recognize it as dimethylarsinic acid derivative whereby one of the methyl groups is substituted with $–AsR_2(=O)$. The systematic name for H_2AsOH is arsinous acid (IUPAC Blue Book [3], P-67.1.1.1) which means that $–AsMe_2(=O)$ substitution is known by the prefix dimethylarsinoyl (IUPAC Blue Book [3], P-67.1.4.1.1.2). The systematic name of our substance is therefore (dimethylarsonyl)dimethylarsinic acid.

Often there is more than one way to construct a systematic name of a substance and one can recognize this substance not as a modified dimethylarsinic acid but rather as arsinic acid with two distinct substitutions: a methyl group and (dimethylarsoryl)methyl group, which takes its name from the arsoryl prefix for –As(=O)< (IUPAC Blue Book [3], P-67.1.4.1.1.2). Thus, one can also name this substance as ((dimethylarsoryl)methyl)(methyl)arsenic acid, although this might look like a computer-generated name. An effective way to check the accuracy of the name is to use it against open-source name-to-structure generators such as one available from www.openmolecules.org. Alternatively, if you have a luxury of knowing several nomenclature experts, ask them independently to name your compound. If they provide the same name, and it generates your structure, chances are you are on the right track.

This article is the solution to the Analytical Challenge to be found at. https://doi.org/10.1007/s00216-022-04116-1.

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Table 1 Identification of ESI-HRMS/MS product ion masses from the pseudo-molecular ions of the mystery substance [1] along with its three main thiolated reaction products

Unknown compound			Monothiolated derivative			Dithiolated derivative			Trithiolated derivative		
Ion mass (*m/z*)	Molecular formula	Neutral loss	Ion mass (*m/z*)	Molecular formula	Neutral loss	Ion mass (*m/z*)	Molecular formula	Neutral loss	Ions (*m/z*)	Formula	Neutral loss
258.9291	$C_4H_{13}As_2O_3^+$		274.9054	$C_4H_{13}As_2O_2S^+$		290.8830	$C_4H_{13}As_2OS_2^+$		306.8600	$C_4H_{13}As_2S_3^+$	
240.9186	$C_4H_{11}As_2O_2^+$	H_2O	256.8958	$C_4H_{11}As_2OS^+$	H_2O	272.8729	$C_4H_{11}As_2S_2^+$	H_2O	272.8727	$C_4H_{11}As_2S_2^+$	H_2S
228.9182	$C_3H_{11}As_2O_2^+$	CH_2O	228.9186	$C_3H_{11}As_2O_2^+$	CH_2S						
210.9077	$C_3H_9As_2O^+$	CH_4O_2	210.9077	$C_3H_9As_2O^+$	CH_4OS	226.8852	$C_3H_9As_2S^+$	CH_4OS	226.8852	$C_3H_9As_2S^+$	CH_4S_2
						168.9121	$C_2H_6AsS_2^+$	C_2H_7AsO	168.9121	$C_2H_6AsS_2^+$	C_2H_7AsS
164.8661	$CH_3As_2^+$	$C_3H_{10}O_3$	164.8661	$CH_3As_2^+$	$C_3H_{10}O_2S$						
			150.9556	$C_3H_8AsS^+$	CH_5AsO_2	150.9559	$C_3H_8AsS^+$	CH_5AsOS	150.9556	$C_3H_8AsS^+$	CH_5AsS_2
138.9734	$C_2H_8AsO_2^+$	C_2H_5AsO	138.9733	$C_2H_8AsO_2^+$	C_2H_5AsS	154.9503	$C_2H_8AsOS^+$	C_2H_5AsS	170.9278	$C_2H_8AsS_2^+$	C_2H_5AsS
136.9578	$C_2H_6AsO_2^+$	C_2H_7AsO				136.9400	$C_2H_6AsS^+$	C_2H_7AsOS	136.9401	$C_2H_6AsS^+$	$C_2H_7AsS_2$
118.9838	$C_3H_8As^+$	CH_5AsO_3				118.9838	$C_3H_8As^+$	CH_5AsOS_2	118.9839	$C_3H_8As^+$	CH_5AsS_3
104.9683	$C_2H_6As^+$	$C_2H_7AsO_3$	104.9684	$C_2H_6As^+$	$C_2H_7AsO_2S$	104.9685	$C_2H_6As^+$	$C_2H_7AsOS_2$	104.9684	$C_2H_6As^+$	$C_2H_7AsS_3$

Declarations

Conflict of interest The authors declare no competing interests.

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