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Simultaneous Determination of Inorganic and Organic Thallium by Atomic Absorption Analysis

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In view of the recent demonstration by HUBER et al. (1978) that thallium (Tl) undergoes biomethylation in sediment, it is anticipated that the product dimethylthallium species (DMT-X) will be studied in greater detail in the near future. In order to demonstrate biomethylation of Tl, HUBER and co-workers measured DMT using a colorimetric procedure involving prior masking of Tl(I) with EDTA. We now report an atomic absorption method which can be used to quantitate inorganic and organic thallium from the same sample.

Perhaps the most useful analytical tool for quantitative determination of inorganic Tl is the atomic absorption method of CURRY et al. (1969) which involves chelation of Tl(I) and (III) with sodium diethyldithiocarbamate (NDDC), followed by extraction into methylisobutylketone (MIBK). The MIBK solution is aspirated directly into an air-acetylene flame and absorbance is measured at 276.8 nm.

Our studies have shown that the above procedure actually measures total thallium, i.e. inorganic and organic. In contrast to some of the stable methylated forms of other metals such as Hg, Pb, and Se, $(CH_3)_2$-Tl-X species are not gases but very stable salts with chemical properties very much like the corresponding inorganic compounds. The key to separation of Tl and DMT resides in the fact that DMT salts are not readily soluble in organic solvents like MIBK, unless chelated with NDDC. Conversely, inorganic Tl can be treated with bromine-water to form $TlBr_3$ which can be extracted directly into MIBK without chelation.

EXPERIMENTAL

Dimethylthallium nitrate. The bromide salt (97-99% , Organometallics, Inc. East Hampshire, NH) which is insoluble in water, was converted to the hydroxide and then to the nitrate by the method of SHIER and DRAGO (1966). A stock soln. containing 10 μg Tl (III)/ml was prepared by dissolving 14.5 mg DMT-NO_3 in 1.0 L distilled water and was stored in polypropylene, since glass markedly absorbs thallium (ZITKO et al. 1975).

Thallium bromide. This bromide salt (99%, Aldrich, Milwaukee, WS) is only slightly soluble in water. For higher concentrations than those used here, the nitrate salt is recommended. A stock soln. containing 10.0 μg Tl(I)/ml was prepared by stirring 13.9 mg TlBr in 1.0 L hot distilled water. This soln. was shaken before each use.

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Thallium standard. A standard can be prepared by direct dissolution of $TlBr_3$ in MIBK. However, this salt is difficult to obtain and rather expensive. An alternative compound which is also directly soluble in MIBK is dimethylthallium phenoxide. In this synthesis, DMT-Br was converted first to the hydroxide and then to the phenoxide by the method of SHIER and DRAGO (1966). A standard soln. was prepared by dissolving 53.28 mg DMT-phenoxide in 1.0 L water-saturated MIBK. Further dilution (1:10, MIBK) yields 3.33 μg Tl/ml. As previously mentioned, these solutions were stored in plastic.

Bromine-water. Saturated.

5-Sulfosalicylic acid. 10% w/v, aqueous.

NDDC. 1.0% w/v sodium diethyldithiocarbamate, aqueous.

MIBK. Methylisobutylketone (4-methyl-2-pentanone), Tech. grade.

BCG. 0.1% w/v brom cresol green, aqueous.

NaOH. 2.5 N soln., 100 g/L H_2O.

ANALYTICAL PROCEDURE

TABLE 1

Sample preparation for determination of inorganic and organic thallium concentration.

	Reagent or Procedure		Sample[a]						
			Blank	A	B	C	D	E	F
1.	distilled water	(ml)	4	3	3	3	3	3	3
2.	10 μg Tl(I)/ml stock	(ml)	0	1.0	0.8	0.6	0.4	0.2	0
3.	10 μg Tl(III)/ml stock	(ml)	0	0	0.2	0.4	0.6	0.8	1.0
4.	bromine-water	(drop)	2	2	2	2	2	2	2
5.	10% sulfosalicylic acid	(drop)	2	2	2	2	2	2	2
6.	H_2O-saturated MIBK	(ml)	3	3	3	3	3	3	3
7.	centrifuge (2500 rpm/10 min)		+	+	+	+	+	+	+
8.	Organic layer; analyze[b]		+	+	+	+	+	+	+
9.	aqueous layer; designate as......		G	H	I	J	K	L	M
10.	BCG indicator soln.	(drop)	1	1	1	1	1	1	1
11.	Adjust pH	(7-8)	+	+	+	+	+	+	+
12.	NDDC soln.	(ml)	0.5	0.5	0.5	0.5	0.5	0.5	0.5
13.	H_2O-saturated MIBK	(ml)	3	3	3	3	3	3	3
14.	centrifuge		+	+	+	+	+	+	+
15.	organic layer; analyze[b]		+	+	+	+	+	+	+

[a] All samples were prepared in labelled test tubes in triplicate, with vortexing between each addition.

[b] MIBK solns. were removed via Pasteur pipette, transferred to plastic scintillation vials, and capped tightly until analyzed.

[c] Dropwise addition of 2.5 N NaOH, one drop after first appearance of a royal blue color, is recommended.

The steps used to prepare the standard curve (Figure 1) are listed in Table 1. Unknown aqueous or urine samples can be substituted in place of the standards used in steps 2 and 3 to achieve a simultaneous determination of both forms of thallium. Additionally, omission of steps 4 through 9 will result in determination of total thallium.

The triplicate blanks were combined and used to zero the instrument for the standard soln. and samples A through F. Likewise, the other triplicate blanks (G) were combined and used for the remaining samples.

Instrument and operating conditions. A Perkin-Elmer, model 303 atomic-absorption spectrophotometer, fitted with a 3-slot Boling burner was used. Flue-gases were removed through an overhead chimney. The air-acetylene flame was adjusted to provide a clean blue flame while aspirating water-saturated MIBK. In addition, the following settings were employed: Thallium lamp current, 12 mA; scale, x 1; gain, 5.6; meter response, 2; filter, out; slit, 4; mode, uv; wavelength, 276.8 nm.

RESULTS AND DISCUSSION

As can be seen from Table 2, chelation and extraction efficiencies are essentially quantitative, and reproducibility of the method is excellent. Figure 1, which graphically represents the data in Table 2, demonstrates the linearity of absorption found with both forms of thallium, up to 10 μg/ml, although much higher concentrations could have been used. The correlation coefficient for the Tl(I) line is .997 and the slope .0054. Corresponding values for the DMT line are .999 and -.0055.

TABLE 2

Absorbance values of samples containing decreasing amounts of Tl(I)Br and increasing amounts of $(CH_3)_2Tl(III)NO_3$.

Sample[a]	A_1	A_2	A_3	$A_{\bar{x}}$
Blank	--	--	--	.000
STD 3.33 μg Tl/ml[b]	.060	.061	.059	.060
A	.057	.057	.061	.058
B	.047	.048	.048	.048
C	.039	.034	.038	.037
D	.024	.028	.026	.026
E	.016	.015	.015	.015
F	.004	.006	.005	.005
G (Blank)	--	--	--	.000
H	.002	.002	.002	.002
I	.012	.013	.012	.012
J	.023	.023	.022	.023
K	.033	.033	.035	.034
L	.045	.046	.047	.046
M	.058	.056	.056	.057

[a] For contents of each sample, see Table 1.

[b] The 3.33 μg Tl/ml standard was aspirated directly and not diluted by extraction into 3 ml MIBK as were the aqueous samples.

The above procedure has been repeated on samples of undiluted rat urine to which quantities of Tl and DMT were added. The results were equivalent to those shown here. Additionally, since hydrobromic acid (HBr) is often used in conjunction with bromine-water to form $TlBr_3$ prior to extraction into MIBK (CURRY et al. 1969), the entire procedure was repeated with this alternate bromination method. The outcome was the same as before, except much larger quantities of 5-Sulfosalicylic acid and NaOH were needed to neutralize the HBr.

The simultaneous determination of inorganic and organic Tl in a given sample represents a significant improvement over current methodology with respect to sensitivity and to expediency, since two distinct species are quantitated in the same sample by atomic absorption spectrophotometry.

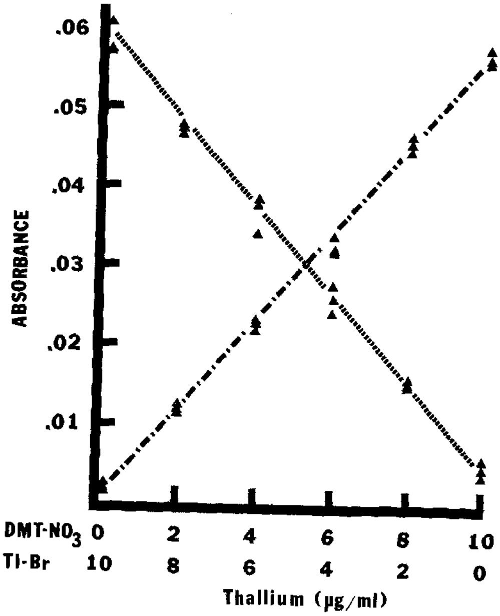

FIGURE 1

Standard curves for the simultaneous determination of Tl(I)Br and $(CH_3)_2$-Tl(III)NO_3 in concentrations from 0 to 1.0 µg/ml in aqueous solutions. The abscissa is labelled with the concentrations of both thallium species added to the test solutions.

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