

perhaps needed to investigate the reasons for this unusual behaviour. In the meantime it is advisable to use DPP with caution in high-resistance solutions.

#### DPASV of Pb and Zn

Several substances capable of sorbing onto mercury occur in natural waters. These include fats, grease, oils, surfactants, detergents, and proteins. The sorption effects of these organics may be expected to be more severe in DPASV than in polarography since the hanging mercury drop electrode (HMDE) commonly used in DPASV allows relatively slow sorption process to reach equilibrium. Despite this fact, few workers have enquired as to how sorption would influence the determination and speciation of trace metals in natural waters using DPASV.

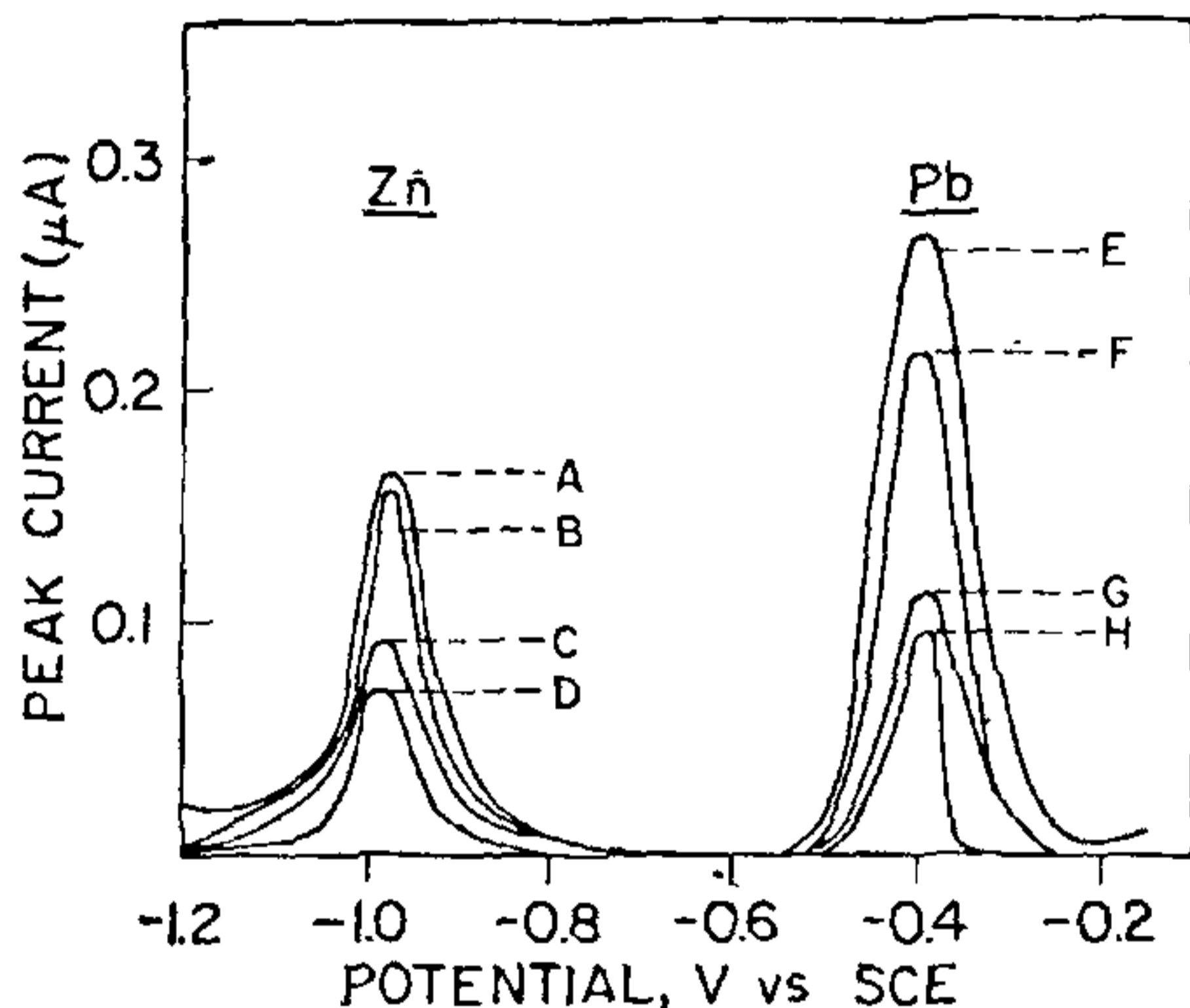


FIG. 2. Effect of camphor on the DPASV of Pb and Zn. Instrumental parameters: plating time, 2 min at  $-1.2$  V vs. SCE. Stripping conditions: pulse amplitude, 25 mV; scan rate, 2 mV/s. Solution: 10 mL Rideau River water sample + 10 mL 1/1F acetic acid/sodium acetate buffer (pH 3.7) + 5 mL camphor of concentration as indicated on each curve (in mg/L): A, 0; B, 1.0; C, 2.0; D, 10-50; E, 0; F, 1.0; G, 10; H, 20-50. Ionic strength, 0.01 (adjusted with  $\text{KNO}_3$ ).

As an example, Figure 2 illustrates the effects of varying concentrations of camphor on the DPASV of Pb and Zn in a sample of Rideau River water. Note that the presence of as low as 10  $\mu\text{g/ml}$  camphor in the sample causes a 50% decrease in the peak current for both Pb and Zn. There was no change in peak potential. Recently, Brezonik *et al.*<sup>9</sup> also observed a decrease in the differential pulse stripping peak current of Cd and Cu in aqueous solutions at pH 3 and 7 in the presence of a number of organic compounds such as agar, starch, Triton-X 100, etc. Two reasons may be advanced for the decrease in  $i_p$ : (i) retardation of the chemical steps prior to electron transfer, thereby

preventing metal deposition; and (ii) the organic layer may change the reversibility of metal oxidation reaction, thereby lowering  $i_p$ . Whatever may be the reason for the decrease in  $i_p$ , the present study shows that sorption effects may present serious problems in interpreting DPASV results on natural waters, especially if the water body is organically rich such as eutrophic lakes, marshes and sewage.

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#### CRYSTALLOGRAPHIC DATA OF $\text{PaT}_5$ , $\text{UT}_5$ AND $\text{UT}_4\text{Cl}$

THREE compounds with chemical formula  $\text{PaT}_5$ ,  $\text{UT}_5$  and  $\text{UT}_4\text{Cl}$  (T = tropolone anion) were synthesized. All the compounds have tetragonal unit cell with lattice parameters  $a = 9.759 \text{ \AA}$ ,  $c = 9.46 \text{ \AA}$ ;  $a = 9.759 \text{ \AA}$ ,  $c = 9.496 \text{ \AA}$  and  $a = 9.695 \text{ \AA}$ ,  $c = 9.552 \text{ \AA}$  for  $\text{PaT}_5$ ,  $\text{UT}_5$  and  $\text{UT}_4\text{Cl}$ , respectively. The Bravais lattice for all is primitive.

Brown and Rickard<sup>1</sup> reported the formation of  $\text{PaT}_4(\text{OEt})$  by the reaction involving lithium tropolonate and the tetrakis (tropolonato) protactinium(V) halides in ethanol. The  $\text{PaT}_4(\text{OEt})$  was also produced when  $\text{PaT}_4$  suspended in ethanol underwent atmospheric oxidation. On the basis of these observations they concluded that the preparation of  $\text{PaT}_5$  is not possible. In 1975 Bagnall, Brown, Bhandari and others<sup>2</sup>, following their success in getting  $\text{UT}_5$ <sup>2</sup>, reinvestigated the protactinium(V)-tropolone system and concluded that the previously reported  $\text{PaT}_4(\text{OEt})$  had been incorrectly characterised and that  $\text{PaT}_4(\text{OEt})$  was in fact  $\text{PaT}_5$ <sup>2</sup>. During their preparation of  $\text{PaT}_5$ ,

TABLE I  
Crystallographic data of  $\text{PaT}_5$ ,  $\text{UT}_5$  and  $\text{UT}_4\text{Cl}$

$\text{PaT}_5$			$\text{UT}_5$			$\text{U}_4\text{TCl}$		
$1/d^2$ obs. ( $\text{\AA}^{-2}$ )	$1/d^2$ calc ( $\text{\AA}^{-2}$ )	hkl	$1/d^2$ obs. ( $\text{\AA}^{-2}$ )	$1/d^2$ calc. ( $\text{\AA}^{-2}$ )	hkl	$1/d^2$ obs. ( $\text{\AA}^{-2}$ )	$1/d^2$ calc. ( $\text{\AA}^{-2}$ )	hkl
0.1366	0.1365	320	0.13825	0.13886	302	0.1399	0.1399	302
0.1467	0.14767	321	0.14837	0.14759	321	0.1703	0.1712	400
0.1686	0.1688	400	0.16860	0.16800	400	0.1753	0.1744	004
0.1770	0.1787	004	0.17703	0.17744	004	0.2512	0.2576	422
0.2023	0.20017	331	0.20232	0.20009	331	0.2799	0.2784	501
0.2546	0.25468	422	0.25290	0.25436	422	0.3456	0.3456	404
0.3490	0.34672	404	0.34563	0.34544	404	0.4282	0.4280	620
0.3895	0.3887	424	0.38563	0.38736	424	0.5109	0.5118	444
0.4704	0.4725	630	0.47039	0.47250	630	0.6710	0.6706	516
0.5142	0.5147	444	0.51086	0.51344	444	0.7081	0.7094	554
0.6256	0.6255	553	0.55132	0.55020	515	0.7503	0.7562	218
0.7081	0.7038	554	0.70475	0.70244	554	0.7772	0.7776	605
0.8279	0.8217	752	0.82277	0.82136	752	0.8683	0.8667	900
0.9022	0.9048	009	0.89020	0.89144	824	0.9914	0.9899	319
1.0820	1.0833	419	1.07904	1.07826	772	1.0503	1.0518	914
1.1550	1.1505	1003	1.15491	1.15250	1003	1.1060	1.1007	1010
1.3420	1.3455	658				1.2105	1.2189	807
1.6240	1.6295	1112				1.4466	1.4436	767

$a = 9.759 \text{ \AA}$	$a = 9.759 \text{ \AA}$	$a = 9.695 \text{ \AA}$
$c = 9.46 \text{ \AA}$	$c = 9.496 \text{ \AA}$	$c = 9.552 \text{ \AA}$
P — Tetragonal	P — Tetragonal	P' — Tetragonal

and  $\text{UT}_5$  they also obtained  $\text{UT}_4\text{Cl}$ . X-ray powder diffraction results indicate  $\text{UT}_5$  to be isostructural with  $\text{PaT}_5$  and  $\text{UT}_4\text{Cl}$  isostructural with  $\text{PaT}_4\text{Cl}$ . These being important chelate compounds of Uranium(V) we report here some crystallographic data on  $\text{PaT}_5$ ,  $\text{UT}_5$  and  $\text{UT}_4\text{Cl}$ .

The crystal structure of all the three compounds was determined by powder method using X-ray diffractometer with filtered copper radiation. All the observed reflections were indexed by the method described by Henry *et al.*<sup>3</sup>. The crystallographic results for the compounds  $\text{PaT}_5$ ,  $\text{UT}_5$  and  $\text{UT}_4\text{Cl}$  are given in Table I. The lattice parameters were calculated from higher angle reflections.  $1/d^2_{hkl}$  were recalculated from these lattice dimensions and are included in the table for comparison. It is observed that all the compounds are tetragonal with primitive Bravais lattice (indices are mixed). A comparison of structural data of  $\text{UT}_5$  and  $\text{PaT}_5$  shows that their structures are identical.

All the compounds have comparable unit cell dimensions.

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