bons), 40.8(CH) minor isomer, 165.4(CO_2), 89.4, 87.3, 73.0, 62.4, 41.4, 33.3(ring carbons), 41.4(CH), 64.5(OCH_2), 13.8(OCH_2CH_3), 21.2(Me) ppm. EI-MS, *m/z*, 290(M^+-2CO), 260(M^+-2CO-NO), 245(M^+-2CO-NO-Me), 234(M^+-2CO-NO-Me-CN). **5d**. major isomer, ^1H NMR($CDCl_3$) δ5.9(m, 4H), 4.20(q, 7.2 Hz, OCH_2), 3.69(d, 2.9 Hz, CH), 3.31(m, 2H), 2.35(m, 2H), 2.26(s, C(O) CH_3), 1.27(t, 7.2 Hz, CH_3), 0.85(d, 7.1 Hz, CH_3) ppm; minor, ^1H NMR($CDCl_3$) δ5.9 (m, 4H), 4.19(q, 7.1 Hz, OCH_2), 3.75(d, 2.2 Hz, CH), 3.3(m, 2H), 2.35(m, 2H), 2.27(s, C(O)CH_3), 1.28(t, 7.1 Hz, CH_3), 1.28(t, 7.1 Hz, CH_3), 0.81(d, 7.1 Hz, CH_3) ppm; **5f**(R = Me, Nu = SCH_2CH_2OH), ^1H NMR($CDCl_3$) δ5.60~6.03(m, 4H), 2.90(m, 1H), 2.73(m, 1H), 3.71(br, OH), 3.41(t, 3.5 Hz, OCH_2), 2.66(t, 2.2 Hz, SCH_2), 1.27(d, 9.1 Hz, Me). [{$MeC_6H_6(CH(CN)CO_2Et)$}$Mn(CO)NO(P(OPh)_3)$] yield 81.6%, IR ν_{CO} 1967 cm^{-1}, ν_{NO} 1735 cm^{-1}, ν_{CO_2} 1720 cm^{-1}, ^{13}C NMR($CDCl_3$), δ229.3(CO), 150.1, 128.8, 124.1, 120.1($P(OPh)_3$), 116.4(CN), major isomer, 165.1(CO_2), 88.2, 84.4, 71.9, 60.2, 40.2, 32.9 (ring carbons), minor isomer, 164.6(CO_2), 88.0, 84.0, 71.7, 60.4, 40.6, 32.9(ring carbons), 61.7(OCH_2), 42.5, 42.1(CH), 20.5(Me), 12.9(OCH_2CH_3).

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A Voltammetric Procedure for Determinations of Four Main Constituents in Ancient Coins

Myung-Zoon Czae*, Suw Yong Ly, and Chul Lee

Department of Chemistry, Hanyang University, Seoul 133-791

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Quite often analytical chemists are asked for to analayze several analytes in the same sample or in a set(large numbers) of samples, in many cases, for the exploratory purposes.[1,2] In this laboratory a rapid simple method is required which can be applied to the multicomponent analysis of coin samples for the purposes of pattern recognition. Samples for analysis were ancient coins (1423-1883 A.D.) having chemical compositions,[3] 60-92% copper, 3-26% lead, 0.2-29% zinc, and 0.2-6% tin as the main constituents.

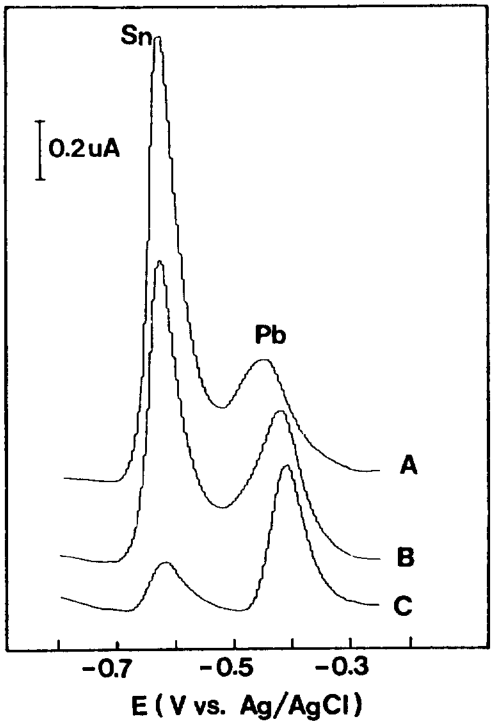

Figure 1. Typical DPAS voltammograms in 0.05 M, pH 8.0 sodium borate solution containing [Sn(IV)] = 2.5×10^{-6} M and [Pb(II)] = 2.7×10^{-7} M, showing the dependance of peak resolution on deposition potentials: A, -1.6V; B, -1.4V; C, -1.2V vs Ag/AgCl. Deposition time, 4 min. Scan rate, 10 mV/sec. Modulation amplitude, 5 mV. Pulse repetition time, 1 sec.

Recently there is a growing appreciation of the power of the pulse voltammetry for it provides multielement capability. It can offer the advantage of simultaneous multi-element determinations (four to six metals) at the lowest costs compared to other competing multianalyte techniques if a suitable experimental procedure is provided.[4]

The one-elment-at-a-time nature of the most existing methods[5,6] and the costs of ICP, X-ray fluorescence analysis[7] and the limited availability of neutron activation analysis and their lacks of sensitivity for(accordingly restriction to) certain metals suggest that the search for an electrochemical multimetal analysis scheme for the alloy samples is timely.

Ideally, a procedure employing only a single technique throughout the entire run is desirable, saying, that can detect the four main elements simultaneously and present their signals to the strip-chart recorder at a time with satisfactory resolutions. However it was not achievable because of the presence of stannic tin, which has peculiar behaviors and shows a great overlapping interference with lead.[8] In this work, as the second best, the advantages of differential pulse polarography(DPP) for copper, lead, and zinc and anodic stripping voltammetry(ASV) for tin are combined.

In most cases(for both DPP and ASV), good chemistry is the proper solution to the resolution problem. One approach is to make choice of a supporting electrolyte medium. Preli-

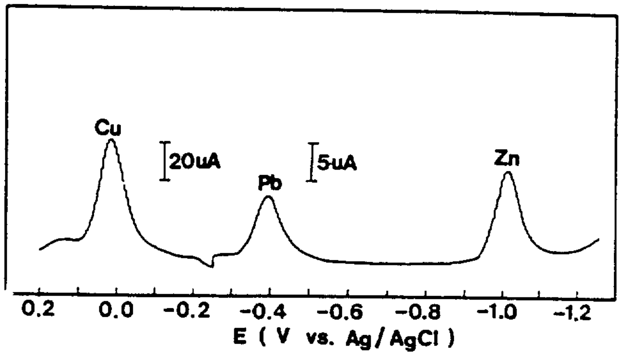

Figure 2. Differential pulse polarograms of a coin sample (No. 49) in 0.05 M sodium borate supporting electrolyte at pH 2.5. Later estimated concentrations: [Cu(II)] = 0.116 mM, [Pb(II)] = 12.6 uM, [Zn(II) = 20.9 uM, and [Sn(IV)] = 2.64 uM. Conditions: scan rate 5 mV/sec, modulation amplitude 25 mV, and pulse repetition time 1 sec.

minary experiments were primarily intended to find out a such medium that (1) can be applicable to both techniques consistently without exchanging and with a minimum of sample solution manipulation, and (2) allows satisfactory separations, between lead and tin in ASV measurement, and in preceeded (or subsequent) DPP measurements for the rest three metals. Although a citrate buffer has been shown[8] to be a medium well suited to the purpose, it was excluded because of the complexity in sample solution manipulation (matrix exchange in the stripping step).

All voltammetric measurements were carried out with an 174A of EG&G PAR as described previously.[9] Stock solutions of metal ions (1.000 g/*l*) and sample solutions (0.06–0.13 g/50 m*l*) were prepared by dissolving drilled chips of the pure metals and sample coins respectively in acids as directed.[5] Temperature of the solution was laboratory ambient (24 ± 2 °C).

A typical stripping voltammogram of a synthetic solution showing a good resolution of tin and lead peaks in sodium borate medium is presented in Figure 1. At low deposition potential (C), the two peaks are well resolved(more than 200 mV) with a lower sensitivity of tin which would be ascribed to a low efficiency of the reduction step, as in citrate buffer.[8] In practice, however, more negative potential (B or A) was found to be more preferable owing to another decrease in sensitivity due to the formation of Cu-Sn intermetallic compound, the effect of which is alleviated by using the generalized standard addition method.[10] Sodium borate medium (0.05 M, pH 2.0–2.5 this time) offers also proper DP polarograms with good separations between analytical peaks and especially copper peak from the sloping portion of the base line(the latter advantage was lost in the case of strongly acidic solution, 0.1 M HCl), demonstrated as in Figure 2.

As the result, the following procedure is proposed: pipet 10 m*l* of 0.05 M sodium borate solution and a 50 u*l* aliquot of sample solution into the electrochemical cell. Adjust pH between 2.0–2.5 with dilute nitric acid(or sodium hydroxide). After de-oxygenation for 10 min, obtain DP polarograms selecting the following working parameters: initial potential, 0.2V; scan rate, 5 mV/sec; scan range, 1.5V; drop time, 1 sec; and modulation amplitude, 25 mV. Subsequently, just adjust pH again to 7.6–8.0 with NaOH for the ASV run. After de-oxygenation for 2 min, start the stirrer and deposition step applying −1.4V for 4 min. After 30 sec resting period, anodic scan is started at the following conditions: scan rate 10 mV/sec; drop time 1 sec, modulation amplitude 5 mV.

For the quantitations, general standard addition method (GSAM) is recommanded in ASV, whereas the external standards (using a calibration curve) are used in the DPP. Two standard additions of tin are made first and then two additions of copper are done keeping the coverage of the response surface in mind. Calculate the results by the total difference calculations-*g.s.a.m.* If the simple standard addition method is to be used in the DPP(as in the small samples case), it may be followed the ASV. Work is in progress in this laboratory to elaborate the method and for a deeper rationale behind it.

The method bias of the proposed procedure was evaluated by analyzing 10 samples and comparing the measurements by neutron activation analysis as the reference method. The t-values(at the 0.05 significant level) were 1.88, 1.60, 1.98 and 2.01 for Cu, Pb, Zn and Sn respectively showing no difference between the two methods.

In conclusions, a simple, rapid electrochemical method has been developed for the multianalyte (four) analysis of ancient coins. The use of sodium borate as a supporting electrolyte permits the simultaneous determination of copper, lead and zinc by DPP and subsequent ASV determination of tin consecutively without medium exchange. Good agreement with neutron activation analysis data confirms the accuracy, efficiency and the applicability of the proposed procedure to multicomponent analysis of copper-base alloy samples with a minimum of sample solution manipulation.

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A New Route to N-Substituted Aminomethylphosphonates

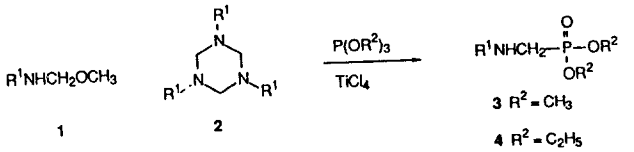
Hyun-Joon Ha*, Gong-Sil Nam, and Kyong Pae Park

Division of Chemistry,
Korea Institute of Science and Technology, Seoul 136-791

Received August 27, 1990

Some of N-substituted aminomethylphosphonic acids and their esters are known to have herbicidal and fire-proofing applications.[1] Synthesis of their acids has been developed in a wide variety of methods.[2,3] However, synthetic methology of their esters is relatively rare. Only two methods were reported for the preparation of their esters: (1) substitution of chloromethylphosphonates[3] or phosphonomethyltriflates[4] with primary amines (2) rearrangement of P-(halomethyl)-N-phenylphosphonoamidates.[5] These are not generally applicable for diverse N-substituted aminomethylphosphonates.

We recently described that condensation of N-substituted N-methoxymethylamines (**1**) with trialkylphosphites affords N-substituted aminomethylphosphonates (**3**,**4**).[6] The reaction of N-substituted amine with paraformaldehyde and sodium methoxide in methanol yields either N-substituted N-methoxymethylamine (**1**) or 1,3,5-trisubstututed-hexahydro-1,3,5-triazine[7] (**2**) depending on the substituent R^1.[8] The heating of **1** under reduced pressure results in a quantitative transformation into the corresponding **2**. In this communication we present a new route to the synthesis of **3** and **4** involving the reaction of **2** with tialkylphosphites in the presence of $TiCl_4$.[9] (Scheme 1)



Scheme 1.

Typical reaction procedure is as follows. To a stirred solution of 1,3,5-trisubstituted-hexahydro-1,3,5-triazine (**2**) (6 mmol) in 100 m*l* of CH_2Cl_2 under nitrogen was slowly added $TiCl_4$ (21 mmol) at 0 °C. After being stirred for 10 min. trialkylphosphite (18 mmol) was added. The resulting solution was stirred at 0 °C for 1-2 hr. After being observed that all starting material was consumed on TLC the reaction mixture was poured into water. The resulting solution was neutralized with sat. $NaHCO_3$ solution. The reaction product was extracted with CH_2Cl_2. Organic layer was washed successively with water and brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The reaction product was further purified by column chromatography or short-path distillation. Results are summarized in the Table 1.

This methods is widely applicable to the various N-substituted aminomethylphosphonates including simple alkyl (entry 1,2,3), bulky t-butyl (entry 4), allyl (entry 5), cyclohexyl (entry 6,7), phenyl(entry 8), benzyl (entry 9) as substituents. Furthermore, a commericial herbicide N-phosphonomethylglycine[10] is also accessed by this method[9] as its corresponding trialkylesters (entry 10,11).[11,12]

The mechanism of this reaction is not clear. But, α-methyleneamine peaks in ^1H and ^{13}C NMR were observed by mixing 1,3,5-trisubstituted-hexahydro-1,3,5-triazine and $TiCl_4$.[13] The observed peaks were close to those of free N-substituted methyleneamine[14] generated by flash vacuum thermolysis of the corresponding N-substituted aminoacetonitrile. Moreover, the color of this mixture became deep wine-red, which indicated that formation of α-methyleneamine complex with $TiCl_4$. On the basis of the observations we predict that this reaction is proceeded by

Table 1. N-Substituted Aminomethylphosphonates Prepared from the Reaction of 1,3,5-Trisubstitutedhexahydro-1,3,5-Triazines with Trialkylphosphites in the Presence of Titanium Tetrachloride

Entry	R^1	R^2	Yield[a,b] (%)	^1H NMR($CDCl_3$)[c]	IR (cm^{-1}, P=O)
1	CH_3CH_2	C_2H_5	49	3.16(d, 10 Hz)	1256
2	$CH_3(CH_2)_2CH_2$	CH_3	65	3.17(d, 12 Hz)	1249
3	$CH_3(CH_2)_2CH_2$	C_2H_5	69	3.00(d, 12 Hz)	1239
4	$(CH_3)C$	C_2H_5	45	3.83(dd, 10 Hz, 5 Hz)	1239
5	CH_2CHCH_2	C_2H_5	60	2.94(d, 10 Hz)	1255
6	Cyclo-C_6H_{11}	CH_3	45	3.06(d, 10 Hz)	1255
7	Cyclo-C_6H_{11}	C_2H_5	48	3.10(d, 10 Hz)	1253
8	Ph	C_2H_5	80	3.54(dd, 12 Hz, 6 Hz)	1212
9	$PhCH_2$	C_2H_5	35	3.15(d, 10 Hz)	1257
10	$C_2H_5O_2CCH_2$	CH_3	92	3.17(d, 12 Hz)	1239
11	$C_2H_5O_2CCH_2$	C_2H_5	65	3.05(d, 12 Hz)	1238

[a] Yield of isolated pure product, not optimized except entry 10. [b] Satisfactory microanalyses obtained. [c] Chemical shift of two methylene protons between nitrogen and phosphorus, referenced by TMS.