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A HIGH-SPEED METHOD OF CONTINUOUS BACKGROUND CORRECTION IN ATOMIC ABSORPTION SPECTROMETRY. III. DIRECT DETERMINATION OF TRACE METALS IN SEA WATER USING THE VARIAN TECHTRON CARBON ROD ATOMIZER, MODEL 63

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A High-Speed Method of Continuous Background Correction in Atomic Absorption Spectrometry. III. Direct Determination of Trace Metals in Sea Water using the Varian Techtron Carbon Rod Atomizer, Model 63

T.H. Donnelly, J. Ferguson and A.J. Eccleston

A newly developed method of background-correction for atomic absorption spectrometry (AAS) combined with the Varian Techtron Carbon Rod Atomizer, Model 63, has been applied to the direct determination of Pb, Zn, Fe, Cu, Ni, Co and Cd in sea water. The background-corrected absorption measurements are reproducible and have a linear relationship to increasing additions of the metal over the ranges examined for the direct determination of metals in sea water. The values are comparable to those obtained by the accepted APDC/MIBK, flame-AAS method, within the limits of precision expected. However, except for Fe and Zn, the method is not sensitive enough to allow measurements at the lower concentration ranges of the metals in sea water. The direct method is a rapid technique for analysing marine waters enriched in metals.

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TABLE 1

Element	Range of Metal Concentration in Sea Water[a] (µg/l)	Detection Limits (for 5 l samples in dilute acid) This work[b].	Parker[c]	Characteristic Concentration[d] (µg/l) CRA Model 63/BCA system	
				Sea Water	Dilute Acid
Pb	0.03 - 9	1	1	1.8	1.4
Zn	0.6 - 33	0.04	0.02	0.3	0.01
Fe	10 -100	0.5	0.6	1.1	0.5
Cu	1 - 20	0.6	1	2.0	0.6
Ni	0.07 - 7	3	2	3.6	3.0
Co	0.04 - 0.7	2	1	2.0	2.0
Cd	0.02 - 0.17	0.02	0.02	0.18	0.05

a. Soluble plus particulate, data from Riley[5].

b. Determined detection limits defined on the basis of a signal-to-noise ratio of 2.

c. Data from Parker[4] for the CRA Model 63.

d. Characteristic concentration[17], frequently, but incorrectly, called "Sensitivity". Defined as weight of analyte element which produces an absorbance of 0.0044.

INTRODUCTION

A high-speed method of obtaining background-corrected absorption (BCA) in atomic absorption spectrometry (AAS) has been[1] developed and its use with graphite furnaces of the L'vov-type[2] assessed[3]. As discussed previously[3], nonatomic absorption (NAA) and light scattering from the matrix are usually much larger in flameless-AAS than in conventional flame-AAS metals but detection limits for the determination of metals[4] (Table 1) are at least 3-4 orders of magnitude lower with the graphite furnace. Comparison of these detection limits with the corresponding metal concentration ranges in sea water[5] (Table 1) indicates that, with the exception of Co, the direct determination of these trace metals in sea water by flameless-AAS methods should be feasible.

The determination of trace metals in sea water by flame-AAS generally involves the extraction of metals into a matrix which does not interfere with the absorption measurement - e.g. by chelate-solvent extraction[6-8], chelate precipitation[9], or chelate ion-exchange separation[10,11]. The direct use of flameless-AAS has hitherto been limited by the difficulty of effectively compensating for the large NAA caused by the sea water matrix. Segar and Gonzalez[12] have examined the use of a Perkin-Elmer 403 AAS, with Perkin-Elmer HGA-70 graphite atomizer and deuterium arc background-corrector, to provide similtaneous background correction for the direct determination of trace metals in sea water. They found, however, that using 20 μl aliquots of sea water and temperatures > 1100 °C the background correction capability of the instrument was far exceeded by the NAA from the salts in the sea water. An alternative approach involving selective volatilization and resolution and identification of the metal absorbance peak was also investigated by the same authors[12]. They found, however, that only Fe could be satisfactorily determined in unpolluted sea water because covolatilization losses of Cu, Mn, Co, Ni, and V occur as the major salts are volatilized at lower temperatures.

The aims of the present study were to examine (1) the use of a newly developed BCA method with miniature type graphite furnaces such as the Varian Techtron Carbon Rod Atomizer, Model 63 (hereafter called CRA Model 63), (2) the effect of using BCA with a electronic response time greater than the absorption signal half-life, and (3) the feasibility of the direct determination of trace transition metals in sea water using the CRA Model 63/BCA system.

I. EXPERIMENTAL

A. Instrumentation

Details of the instrumentation for BCA measurements have been given previously[1,3]. Unless otherwise stated, the BCA system was used in conjunction with the Varian Techtron Carbon Rod Atomizer Model 63, and the output recorded on a Varian Recorder Model A.25 (0.5 sec pen response).

Preliminary work was carried out using a Varian Techtron Carbon Rod Atomizer Model 61, but because of significant improvements in the design of the Model 63, the results from this instrument only are presented. These improvements include (1) a slightly increased size of the graphite furnace which allows a 5 μl aliquot to be injected using a device such as the Oxford Sampler*, Autopette+, or Eppendorf‡ pipette, and (2) the use of pyrographite-coated furnaces, giving higher resistance to oxidation and

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* Oxford Sampler, Oxford Laboratories, San Mateo, California, U.S.A.

+ Autopette, A.E. Stanton, 121 Rickett Road, Mt. Waverley, Melbourne, Victoria.

‡ Eppendorf, Geratebau, No. 2 Hamburg 62, P.O. Box 630324, West Germany.

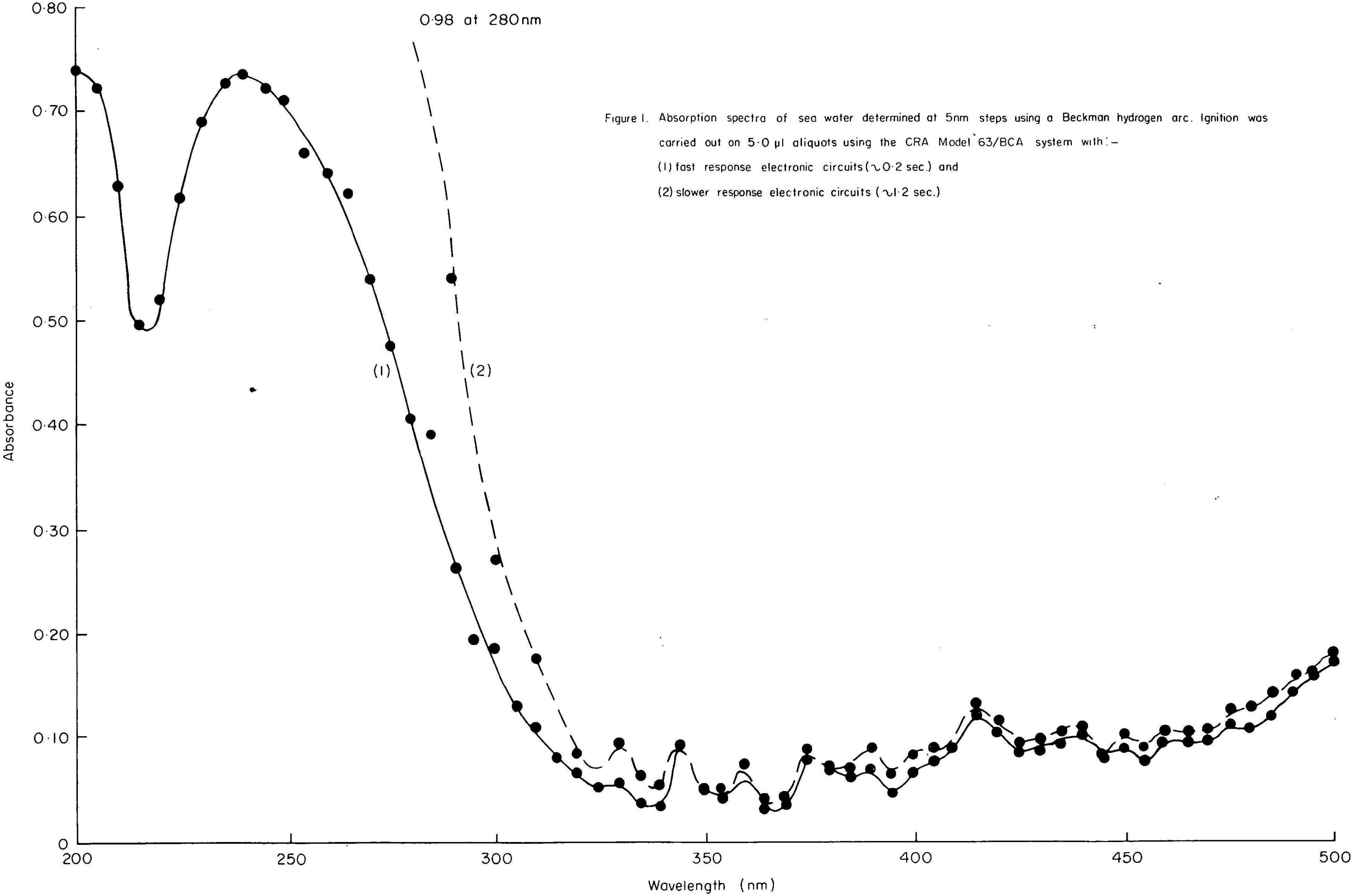

Figure 1. Absorption spectra of sea water determined at 5nm steps using a Beckman hydrogen arc. Ignition was carried out on 5·0 µl aliquots using the CRA Model 63/BCA system with:–

(1) fast response electronic circuits ($\sim$0·2 sec.) and

(2) slower response electronic circuits ($\sim$1·2 sec.)

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consequently longer working life. Aspila <u>et al</u>.[13] have discussed the advantages of using pyrographite coated furnaces for AAS.

B. Electronic Response Time of BCA Instrumentation

It was found previously[1] that the major time-determining component was the synchronous integrator circuit which in combination with all other components gave a total response time ∿1.2 second. This response time is shorter than the absorption signal half-life of atomic vapour produced using a L'vov type furnace (range 3-5 sec[3]) but is longer than the corresponding range for the CRA Model 63 (0.3-0.8 sec.; private communication. J.P. Matousek, Varian Techtron 1974). In the latter circumstances it is possible that reproducibility and sensitivity of the system may be adversly affected, and these factors were therefore examined using the CRA Model 63/BCA system (during the determination of trace metals in sea water). For comparison a modified synchronous integrator circuit was built (total electronic response time ∿0.2 sec) and the absorption spectrum of sea water determined using both slow and fast response circuits.

C. Absorption Spectra of Sea Water

The spectrum of sea water was determined over the wavelength range 200 to 500 nanometres (nm) in 5 nm steps, using the CRA Model 63 and 5.0 μl aliquots of sea water. Measurement was carried out using the hydrogen lamp in absorbance mode, with both the slow and fast response circuits (Fig. 1).

D. Precision of the BCA Method

The reproducibility of absorbance measurements was determined using an aqueous lead standard and a filtered sea water sample (see below) to which known concentrations of

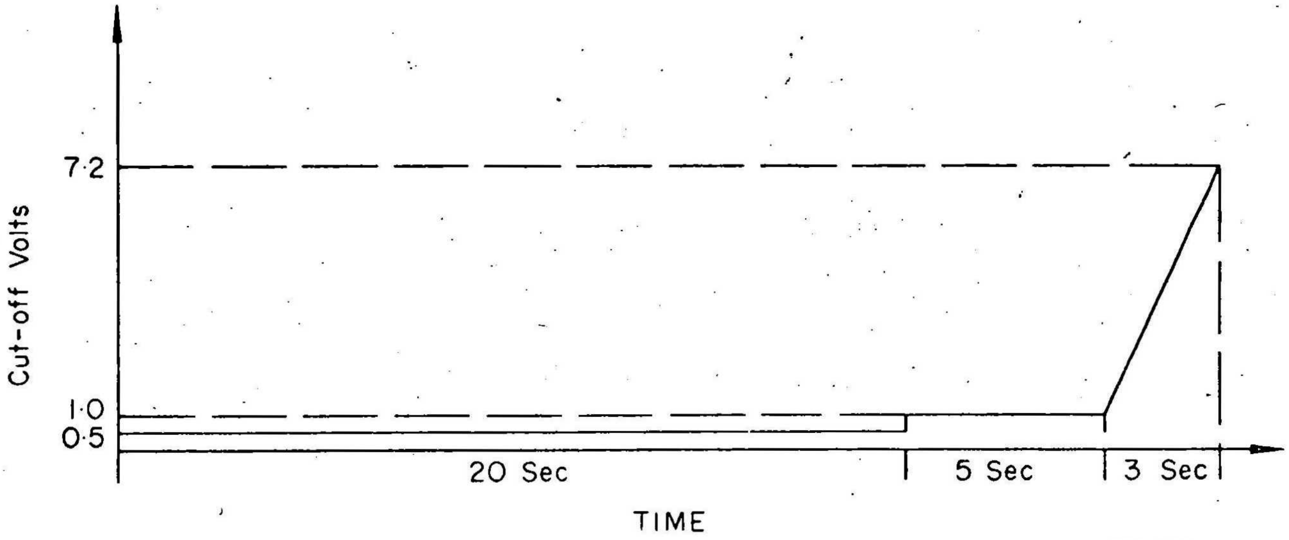

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Figure 2. Heating cycle (Ramp Mode) used on the CRA Model 63 for the determination of trace metals in sea water.

TABLE II

Element	Matrix	Concentration (μg/l)	SD (μg/l)	RSD (%)
Ni	MIBK extract	50	± 3.3	6.5
Pb	0.1 N HCl	50	± 2.0	4
"	Urine[a]	150	± 6.0	4
"	Sea Water	50	± 4.8	9.5
Cu	" "	90	± 7.0	8.0
Cd	" "	4	± 0.4	10.0

a. Data from Stevens et al.[15]. Total salt concentration in urine is about one-tenth that in sea water.

TABLE III

Gas Flow to Furnace: N_2 - usually near maximum of flowmeter, 61/min;
: H_2 - 0.91/min

Heating conditions shown in Fig. 2.

Element	Wave length of Resonance Line (nm)	Spectral Band Pass (nm)	Spectral Lamp Current (mA)	Gain (Max Gain = 800V)
Pb	217.0[1]	0.33	4	200
Zn	213.9	0.33	3.5	200
Fe	248.3	0.17	3	280
Cu	324.8	0.33	1.5	160
Ni	232.0	0.08	3	280
Co	240.7	0.08	3	480
Cd	228.8	0.33	3	160

[1] Superior to the 283.3 nm line because of the low noise levels obtained with the Model 63/BCA system.

Pb, Cu, and Cd were added. Sets of ten repeat measurements in BCA mode were used to obtain relative standard deviations (RSD) (Table II).

E. Determination of "Dissolved" Trace Metals in Sea Water

The sea water sample used in this study is a surface sample collected from close to the shore at Batemans Bay, N.S.W., Australia. It was stored in polythene containers for several weeks after collection, and immediately before use it was filtered through a 0.45 μm Millipore filter.

1. Direct determination of trace metals in sea water using the CRA Model 63/BCA system.

The operating conditions for the direct determination of trace metals in sea water using the CRA Model 63/BCA system are shown in Table III. The furnace heating cycle is shown diagrammatically in Fig. 2. A fixed cut off voltage was suitable for all determinations of metals in sea water and sensitivities were better with the "ramp" as compared to the "step" heating mode. The N_2 and H_2 gas flow to the CRA needed very little adjustment. The H_2 flow was kept constant at 0.9 l/min; the N_2 flow was generally maintained near 6 l/min to increase the lifetime of the graphite furnace, but was occasionally lowered to improve element sensitivity to the values shown in Table I. Up to 200 μl aliquots of multi-metal standard solutions were added to three 10.0 ml samples of filtered sea water, or filtered sea water acidified with 0.15 ml of 12N HCl. 5.0 μl aliquots of each solution were then pipetted into the graphite furnace, and the absorption determined in BCA mode. Results for acidified and non-acidified samples were not significantly different.

2. Chelate-solvent extraction of metals from sea water.

The ammonium tetramethylenedithiocarbamate-methyl isobutyl ketone (APDC-MIBK) solvent extraction technique described by Brewer et al.[6] was used. Four samples, three of which contained suitable additions of a multi-metal standard, were extracted twice, and metal concentrations in the MIBK layers determined using the CRA Model 63/BCA system, or with conventional flame-AAS methods, also with BCA. In the former case sea water to MIBK ratios of 20:1 rather than 40:1 were used, and volatilization conditions adjusted to reduce sensitivity. "Blank" values, as indicated by the metal concentrations in MIBK from the second extractions, were never greater than 5% of the total. Addition of HCl to the samples before extraction, as outlined by Brewer et al.[6], did not significantly affect the results.

II. RESULTS AND DISCUSSION

A. Absorption Spectra of Sea Water

With the faster response electronic circuits (total response time ∿0.2 sec) and 5.0 μl aliquots of sea water, the NAA was found to be too large to measure at wavelengths less than 280 nm (Fig. 1). However, using the slower response electronic circuits (total response time ∿ 1.2 sec) the spectrum of sea water could be determined at wavelengths down to at least 200 nm, which covers the range where the resonance lines of most of the metals lie. The slower response circuit was therefore used exclusively for BCA measurements reported in this paper.

In Part 1 of this series[1] the importance of the relationship of the electronic circuit response time to the half-life of the absorption signal was discussed. The following points were made: (1) providing the absorbance does not exceed 1, a long circuit response time does not discard absorption information but presents it at a lower peak amplitude on a longer time base, and (2) if, as in the present investigation, the signal duration is comparable with, or less than, the response time, then the amplitude and pulse shape will be distorted, but as the distortion will be similar for both channels, BCA measurements should be linear for a variety of pulse amplitudes.

The fine structure of the spectrum of sea water measured with the slower response circuit is similar to that shown by Willis[14] for an aqueous solution of 5% NaCl measured by flame-AAS. This is an indication that the degree of distortion is not large. In any event, the distortion of the signal is similar for both channels, and the direct determination of trace metals in sea water, using the CRA model 63/BCA system with the slower response circuit, should be feasible.

B. Reproducibility of a BCA Measurement

Data in Table II indicate that the RSD for lead in dilute acid solution obtained with the CRA Model 63/BCA system (4%) is similar to that reported by Stevens *et al.*[15] using the CRA Model 63 for the determination of Pb in the presence of salt concentrations of the order of 1/10th that of average sea water. Stevens *et al.*[15] did not employ background-correction, but varied the volatilization conditions to resolve the Pb absorbance from other background peaks.

The RSD for Ni in MIBK extracts of aqueous solutions, determined with the CRA Model 63/BCA system, is higher (6.5%; Table II) than that for Pb in dilute acid solutions. This may be a result of lower aliquoting precision and/or "creep" of the MIBK sample from the graphite furnace, caused by the relatively low surface tension of MIBK.

Previous studies have shown that the precision of flameless-AAS is not high under the best of conditions (e.g., absorption measurements without background interference and in the optimum concentration range for low signal to noise ratios). Willis[16] quotes a RSD of 6% for a CRA Model 63 using a disposible tip pipette of the Eppendorf type. If significant NAA occurs, and is measured by checking separate samples with a spectral and a continuum source, then an even higher RSD might be expected.

The RSD for Pb in sea water given in Table II (9.5%) is 2.4 times that for the same concentration of Pb in dilute acid solutions. The RSD values for Cd and Cu are similar to that for Pb. L'vov[2] has indicated that, using his furnace, a RSD ∿ 8% can be expected for metal determinations in matrices producing significant background, even when automatic background correction is used, and on this basis the RSD values of 8-10% obtained in this investigation are not abnormally high.

C. Sensitivity of the CRA Model 63/BCA system

It was pointed out previously that one effect of the use of the slower response electronic circuits may be loss of sensitivity. In Table I detection limit values previously determined[4] are shown for the metals examined in this study. These values were obtained using the CRA Model 63. For contrast the detection limit values for the same metals determined in dilute acid using the CRA Model 63/BCA system are also shown in Table I. The two sets of values are very similar, and indicate that there has been no significant loss in sensitivity from using the BCA measurement system.

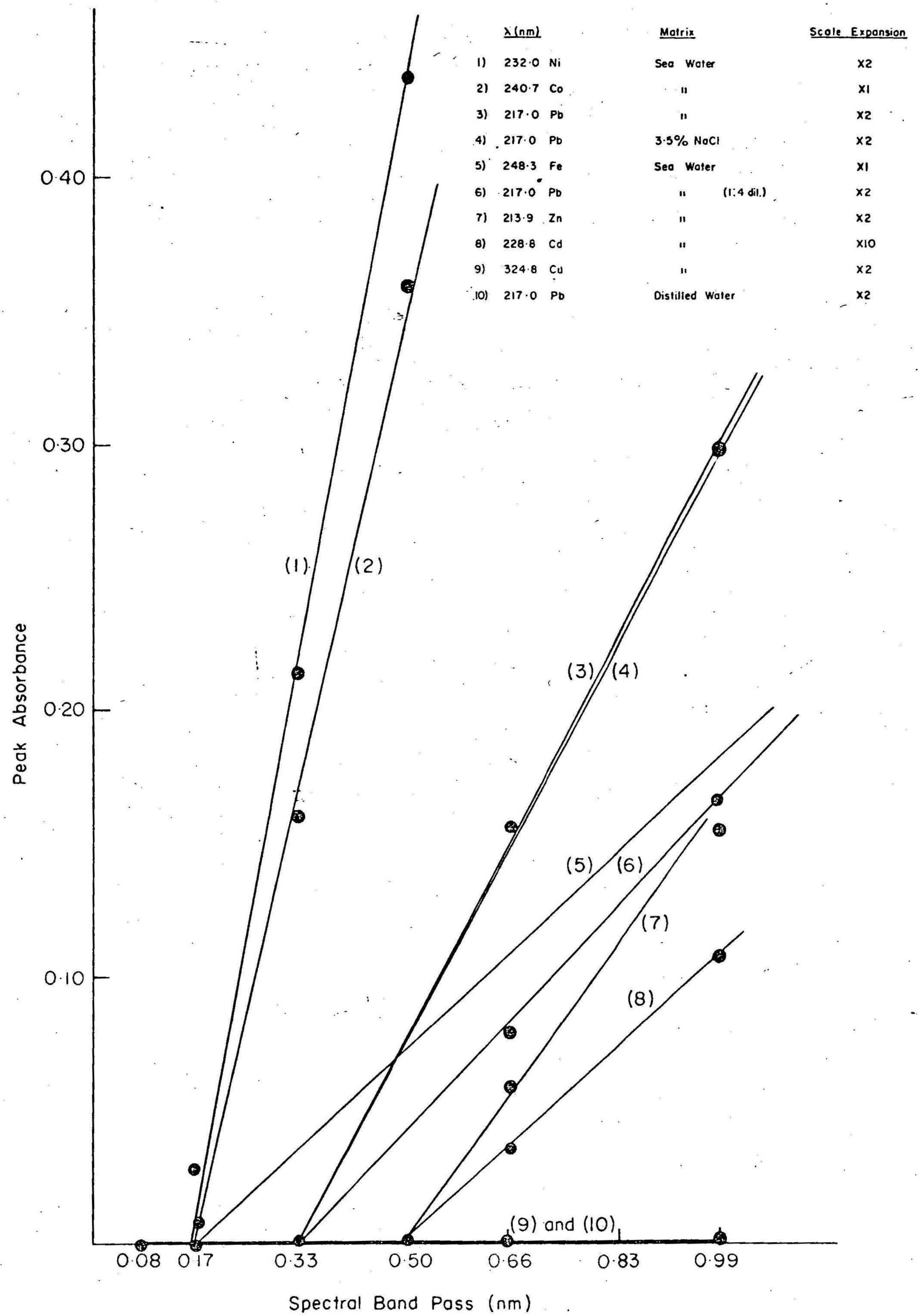

Figure 3. Anomalous absorption versus spectral band pass curves determined during the vaporization of 5·0 µl aliquots of sea water in the CRA Model 63/BCA system.

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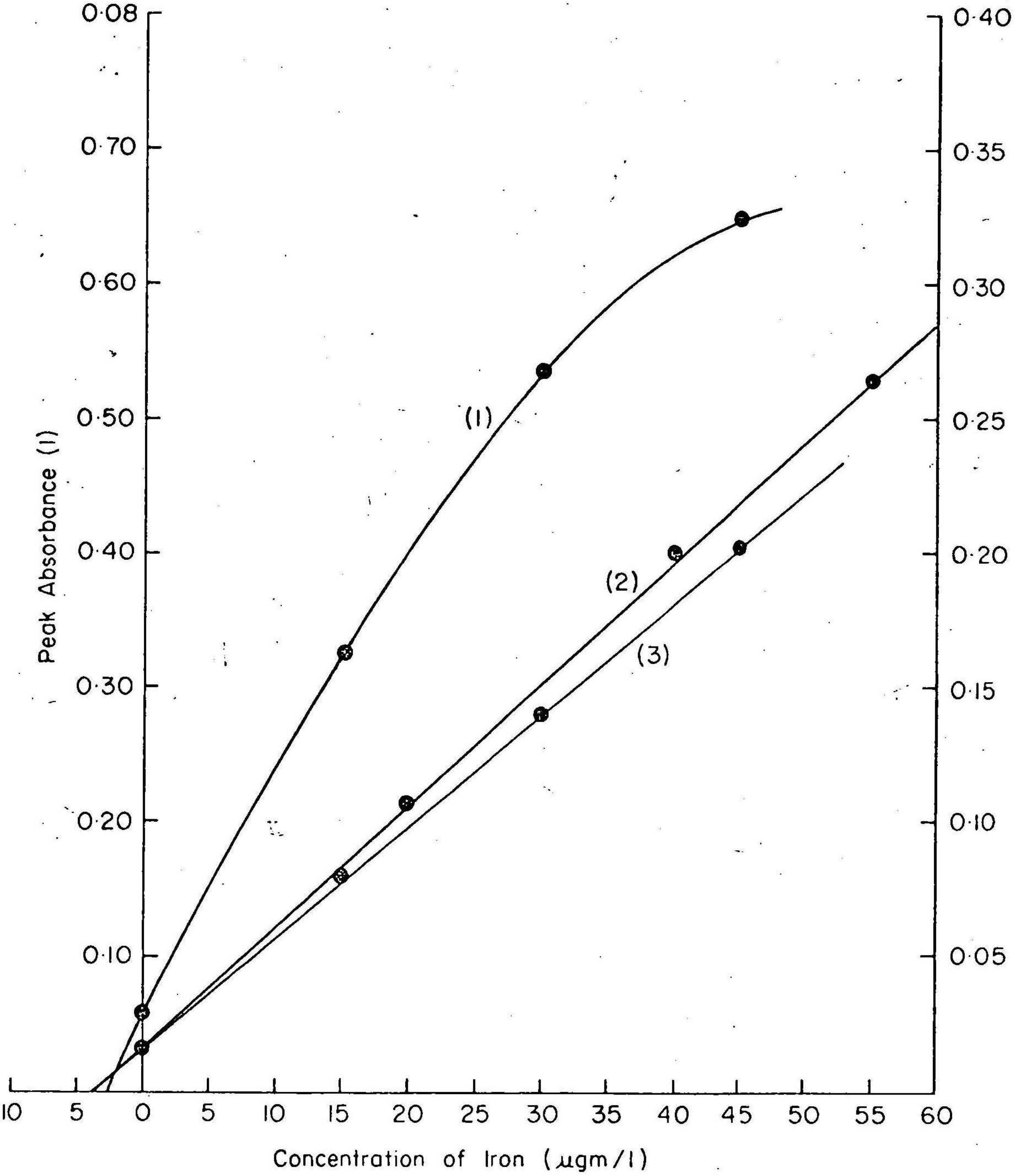

Figure 4. Determination of Fe in the Batemans Bay sea water sample by :-

(1) APDC/MIBK solvent extraction, CRA Model 63/BCA system, for a sea water to MIBK ratio of 20:1,

(2) direct determination of Fe in the sea water sample using the CRA Model 63/BCA system, and

(3) APDC/MIBK solvent extraction, flame-AAS, for a sea water to MIBK ratio of 40:1

However, there are some marked differences in sensitivity between metals determined in sea water and the same metals determined in distilled water. These differences were caused mainly by the need to decrease the spectral band pass (SBP) in the case of Pb, Ni, and Cd when determined in sea water (Fig. 3). Because the signal from the continuum source is proportional to the square of the SBP, and that from the spectral lamp is directly proportional to the SBP, the reduction of SBP reduces the continuum signal much more than the spectral lamp signal. Greater EHT to the photomultiplier is therefore needed to balance the two lamps for BCA measurements. The increased EHT is also the reason why Ni and Co (SBP = 0.08 nm) are less sensitive, in both matrices, when measured using BCA, as contrasted with their detection limit values measured using only the spectral lamp (Table I). The reasons for the considerably lower sensitivity values for Cu and Zn in sea water, compared to dilute acid, have not been determined, but are probably connected with the volatility of the chlorides of these metals, as suggested by Segar and Gonzalez[12].

D. Dependence of BCA on Metal Concentrations

Application of the CRA Model 63/BCA system and the method of standard additions to the direct determination of trace metals in the sea water sample gave linear relations for all the metals examined up to the maximum concentrations used in this study (Pb = 40, Zn = 19, Fe = 55, Cu = 150, Ni = 100, Co = 180, and Cd = 6 μg/l), when metal concentration was plotted against BCA. A typical result illustrating the direct determination of Fe is shown in Fig. 4.

TABLE IV

Element	Direct Measurement using CRA Model 63/ BCA System (µg/l)	APDC/MIBK Solvent Extraction	
		Flame - AAS[a]	CRA Model 63/BCA[b] (µg/l)
Pb	$\leqslant 1.8$	1.5	0.3[c]
Zn	5.0	6[c]	n.d.[d]
Fe	3.5	3.5	2.5[c]
Cu	$\leqslant 2$	1.3	1.3
Ni	< 3.6	0.8	1.0
Co	< 2	0.5	0.5
Cd	$\leqslant 0.2$	0.13	0.2

[a] Sea water : MIBK = 40:1

[b] Sea water : MIBK = 20:1

[c] Significant curvature in concentration versus BCA graphs

[d] Zinc not determined as concentration exceeds the capability of CRA Model 63/BCA system

Plots of BCA versus metal concentration, for measurements on MIBK extracts, were also linear for all flame-AAS determinations (see line 3 in Fig. 4, which shows the determination of Fe). However, when the CRA Model 63/BCA system was used for measurement of metal concentration in the MIBK extracts, the graphs were all curved to various degrees. This curvature is probably partly due to the high metal concentrations in the MIBK extract (up to 20 times those in the original sea water). In the concentration ranges used in this investigation (see above) significant curvature resulted for Fe (Fig. 4, line 1) and Pb.

E. Metal Concentrations in Sea Water

Table IV lists the concentrations of "dissolved" metals in the sea water sample from Batemans Bay found by direct determination using the CRA Model 63/BCA system.

The accuracy of the direct determination is illustrated by comparison with the same metals determined by APDC/MIBK solvent extraction followed by flame-AAS[4] or by CRA Model 63 measurement in the BCA mode. As the time response of the electronic circuits is not significant for flame-AAS, and as it was shown that the effect of the different lamp geometries is also not significant[3], comparison with this established method should be valid. From Table IV it can be seen that for Fe and Zn, which have the sensitivity necessary for their measurement at the lower concentration range of metals in sea water, good agreement is found with the solvent extraction/flame-AAS determination. The metals Pb, Cu, and Cd, when determined near their absolute sensitivities also correspond reasonably well, but where the metal concentration in the sea water sample is below the absolute sensitivity (Ni and Co) no comparison can be made.

In initial experiments on the direct determination of Pb in sea water using the CRA Model 63/BCA system, anomalously high absorbances were found. This occurred when sea water was vapourized by spectral lamp alone, but was not apparent for solutions of Pb in dilute acid. Further investigation of the metals in sea water showed that anomalous absorption by Pb, Zn, Fe, Ni, Co and Cd, but not Cu (Fig. 3), occurred at wide SBP. This effect may result from a very slight interaction between the two variable gain amplifiers (see Fig. 1 in ref. 1), and becomes apparent only under the extreme conditions of the direct determination of metals in sea water. Further investigations of this effect are in progress, but in the present study it was overcome by reducing the SBP below the limits indicated in Fig 3. The SBP values used are shown in Table III, and, except for Pb, Ni, and Cd, are those recommended by Varian Techtron.

Metal determinations using the CRA Model 63/BCA system were also made on MIBK extracts of the sea water sample (sea water: MIBK = 20:1). Comparison with the solvent extraction/flame AAS values (Table IV) shows good agreement for Cu, Ni, Co, Cd and Fe. The discrepancy between the Pb values obtained by the two methods is probably a result of the strong curvature of the Pb concentration versus absorbance graph obtained using the MIBK extract. The concentration of Zn in the MIBK extract was too high to measure with the CRA Model 63/BCA system.

IV CONCLUSIONS

Application of a Varian Techtron CRA Model 63 (absorption signal half-life 0.3 to 0.8 sec) with continuous background-correction, where the total electronic response time is ∿1.2 second, to the determination of trace concentrations of Pb, Zn, Fe, Cu, Ni, Co and Cd in sea water and dilute acid solutions has shown that, although the response time of the electronic system is longer than the residence time of the sample vapour in the light beam, there are no marked adverse effects on the precision, sensitivity, or accuracy of the BCA measurement. Using the CRA Model 63/BCA system it has been shown that, whereas RSD values ∿ 4% can be obtained for metals in dilute acid solution, RSD values of 8-10% are obtained for metals determined in sea water.

The method is suitable for the direct determination of Fe and Zn over the complete concentration ranges reported for sea water, and for the direct determination of Pb, Cu, Ni, Co and Cd concentrations in the higher points of the ranges. Sensitivities sufficient to cover the complete ranges can be achieved by a preliminary chelate-solvent extraction step followed by vaporization of the organic extract. The concentration factors and volume of organic extract are much smaller than those needed for flame-AAS, and consequently smaller sample volumes are required. Compared to the flame and flameless-AAS methods presently available, the CRA Model 63/BCA method is very rapid. This is because of its capacity to compensate for the large NAA present when sea water is vaporized in the graphite furnace, and less optimization of instrument parameters is needed. The direct method requires much smaller sample volumes than those used in the conventional[6] flame-AAS determination of metals in sea water with pre-concentration by chelate-solvent extraction or ion-exchange.

The CRA Model 63/BCA system described in this paper appears to provide the basis for a simple, rapid method for the detection and measurement of abnormally high metal concentrations which, for example, may occur in polluted near-shore sea water or interstitial waters of marine sediments. It would be of particular value for the latter where sample volumes are usually small.

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