Nickel and cobalt determination in the North Western Mediterranean by differential pulse cathodic stripping voltammetry

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Differential pulse cathodic stripping voltammetry can be applied to sea water with high sensitivity for nickel and cobalt analysis (limits of detection about 0.005 and 0.002 μg L⁻¹ respectively) using the dimethylglyoxime complexes. At concentrations of 0.200 μg Ni L⁻¹ and 0.050 μg Co L⁻¹ the standard deviations for replicate analyses were 8% and 2% respectively. The linearity of the calibration curve derived during the method of standard additions was ±5% for Ni and ±1% for Co. Analysis of water from North Western Mediterranean Sea profiles gave Ni levels of 0.207 ±0.043 μg L⁻¹ and Co levels of 0.006±0.003 μg L⁻¹. The metal levels found accorded closely with those reported by other authors in different oceans.

Table
Concentration and distribution of Ni and Co in seawater of different oceanic regions.

<table>
<thead>
<tr>
<th>Authors</th>
<th>Ocean</th>
<th>Analysis method</th>
<th>Conc. (µg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Danielsson and Westerlund (1983)</td>
<td>Indian</td>
<td>Extraction &amp; AAS</td>
<td>Ni 0.30-0.55</td>
</tr>
<tr>
<td>Knauer et al. (1982)</td>
<td>N.E. Pacific</td>
<td>Extraction or Chelex &amp; AAS</td>
<td>Co 0.005-0.092</td>
</tr>
<tr>
<td>Brugmann et al. (1983)</td>
<td>Norwegian</td>
<td>Extraction &amp; AAS</td>
<td>Ni 0.150-0.200</td>
</tr>
<tr>
<td>Mart et al. (1983)</td>
<td>Arctic</td>
<td>Cathodic Stripping Voltammetry</td>
<td>Ni 0.079-0.131</td>
</tr>
<tr>
<td>Bruland and Franks (1983)</td>
<td>N.W. Atlantic</td>
<td>Extraction &amp; AAS</td>
<td>Ni 0.120-0.360</td>
</tr>
<tr>
<td>Yeats and Campbell (1983)</td>
<td>N.W. Atlantic</td>
<td>Chelation-extraction &amp; AAS</td>
<td>Ni 0.222 (mean)</td>
</tr>
<tr>
<td>Bruland and Franks (1983)</td>
<td>N. Pacific</td>
<td>Extraction &amp; AAS</td>
<td>Ni 0.150-0.660</td>
</tr>
<tr>
<td>Boyle and Huested (1983)</td>
<td>E. Pacific</td>
<td>Precipitation &amp; AAS</td>
<td>Ni 0.120-0.660</td>
</tr>
<tr>
<td>Boyle and Huested (1983)</td>
<td>Bering Sea</td>
<td>Precipitation &amp; AAS</td>
<td>Ni 0.36-0.66</td>
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<td>Boyle and Huested (1983)</td>
<td>Circumpolar current</td>
<td>Extraction &amp; AAS</td>
<td>Ni 0.27-0.48</td>
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<tr>
<td>Jickells and Knap (1984)</td>
<td>Bermuda inshore</td>
<td>Extraction &amp; AAS</td>
<td>Ni 0.16</td>
</tr>
<tr>
<td>Jones and Murray (1984)</td>
<td>N.E. Pacific</td>
<td>Extraction &amp; AAS</td>
<td>Ni 0.268 (mean)</td>
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<tr>
<td>Spivack et al. (1983)</td>
<td>Mediterranean</td>
<td>Extraction &amp; AAS</td>
<td>Ni 0.25</td>
</tr>
<tr>
<td>Boyle et al. (1984)</td>
<td>Mediterranean</td>
<td>Extraction &amp; AAS</td>
<td>Ni 0.126-0.289</td>
</tr>
<tr>
<td>Kremling (1985)</td>
<td>Atlantic</td>
<td>Extraction &amp; AAS</td>
<td>Ni 0.194</td>
</tr>
<tr>
<td>This study</td>
<td>N.W. Mediterranean</td>
<td>Cathodic stripping Voltammetry</td>
<td>Co 0.002-0.012</td>
</tr>
</tbody>
</table>

1) direct application without preconcentration to a wide range of natural aqueous solutions;
2) speed;
3) specificity and simultaneity for measurement of cobalt and nickel;
4) non-destructive analysis (hence in principle chemical changes can be made to the solution and the analysis repeated);
5) sensitivity.

We have applied differential pulse cathodic stripping voltammetry for analysing nickel and cobalt in seawater. The metals are adsorbed on the static mercury drop electrode as dimethylglyoxime (DMG) complexes. We followed but modified the procedure described by Pihlar et al. (1981), Weinzierl and Umland (1982), Braun and Metzger (1984), and Torrance and Gatford (1985).

The high sensitivity results from the adsorptive accumulation of the metal-DMG complexes on the mercury drop during a period in which the potential at the drop is held at a value more positive than that required for reduction of the complexes. This accumulation step is followed by a differential pulse voltammetric stripping scan during which the accumulated complexes are reduced.

ANALYTICAL PROCEDURES

Sampling

During the PHYCEMED-2 cruise on 19-20 October 1983, unfiltered sea water samples were collected in conditions identical to those described by Laumond et al. (1982). A Goflo bottle was used in a modified form, and all metal parts except the hydrowire were sealed with Teflon. The samples were taken from on board ship; since it was not possible to row well away from it in a small dinghy or similar craft to avoid contamination, no surface sampling was attempted.

All results in this paper are thus for deeper waters; the literature figures we quote are mostly exclusive of surface waters and relate to depths greater than or equal to 100 m.

Water from the Goflo bottle was run under cover of a protective cone into high density polyethylene bottles previously soaked in nitric acid (20% for five days followed by extensive treatment with ultrapure water (triple distilled). Each bottle was rinsed out four times with the seawater before the sample was accepted. These bottles were not new but had been stored many times previously with seawater, since it is known that new bottles produce erratic and high contamination for some elements.

The samples were not filtered. They were acidified by Suprapur nitric acid to pH 1.5-2 for storage at 4°C and determination of metals.

To measure the oceanic profiles of nickel and cobalt, several samples were collected at stations ET-R2 (42°02N-05°05E) and GY-W (40°00N-06°30E) as shown in Figure 1.

![Figure 1](image)

Location of the profile sampling stations.

Reagents

All the reagents used, such as nitric acid and ammonia solution, were Suprapur Merck analytical reagent grade.

Milli-Q water was used as demineralized water. Standard nickel and cobalt solutions of 0.1 µg L⁻¹ and 0.01 µg L⁻¹ were prepared separately by dilution from Titrisol Merck standard solution.
1% dimethylglyoxime. A 1% solution was prepared from Merck analytical reagent grade in "Spectrosol" ethanol.

Instruments and methods

An EG & G Princeton Applied Research Model 384B Polarographic Analyser was used in conjunction with a model 303 Mercury electrode assembly and a Bausch and Lomb DMP-400 digital plotter.

The static mercury drop electrode used was preferred to the thin film mercury glassy carbon rotating electrode because it was possible to renew the mercury drop before every analytical cycle to avoid possible build-up of non-degradable organic compounds with time which might mask the electro-active surface of the mercury.

Silver wire was used as a reference electrode, platinum wire as the counter electrode, and a 30 ml Teflon cell was used as polarographic cell.

All preparation steps and the other analytical procedures were carried out under strict laminar hood conditions in a semi-clean laboratory.

The actual analytical cycle is standard and similar to those reported earlier (e.g. Mart et al., 1983).

In Figures 2-4 are presented typical peaks and calibration graphs for nickel and cobalt. Total analysis cycle time is 24 minutes.

The concentrations of the elements in the water sample were computed by standard additions. A minimum of three spikes of 0.2 μg L⁻¹ of nickel and 0.02 μg L⁻¹ of cobalt were added to the sample to obtain a linear calibration graph. Because of the good linearity, addition of only one spike was routine thereafter.

Interferences

Torrance and Gatford (1985), who applied differential pulse voltammetry for the determination of nickel (0.8 μg L⁻¹) and cobalt (0.2 μg L⁻¹) in simulated coolant from a pressurized water reactor, investigated the interference effects from other metals such as Fe³⁺ (40 μg L⁻¹), Mn²⁺ (10 μg L⁻¹) and Cr³⁺ (10 μg L⁻¹).

They found no significant effect at the 95% confidence level on the peak heights for nickel and cobalt.

We collected sea water off the Cap d'Ail beach near Monaco and determined the effects of adding various amounts of V⁴⁺, Mn²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Pb²⁺ in excess of the amount of both nickel (roughly 200 ng L⁻¹) and cobalt (roughly 5 ng L⁻¹) independently in two series of experiments. The ratios of amounts added, over the found nickel and cobalt concentrations, were 1.5, 3.0, 6.0, 12 and 24 times. For V⁴⁺ and Mn²⁺ there
was no observable interference effect at any concentration (confidence levels 88 and 92% respectively). With the other elements an effect was noticed at the highest concentration—the peak height of nickel was decreased by about 10%. Also an extra ±2% variability was introduced into the results for the cobalt determination.

The effect of adding another strong complexer, EDTA, was investigated. We added EDTA such that EDTA/DMG ratios of 0.5, 1.0, 2.0, 4.0 and 8.0 were reached. The only result was to increase the variability of analysis by 1% for nickel and 3% for cobalt, at the highest concentration used. This indicates the robustness of the method even in the presence of strong complexing agents other than DMG, and suggests that traces of these in sea-water samples are unlikely to affect results unduly. It also suggests that the use of DMG is likely to complex even relatively strongly bound metal, and probably produces analytical figures which represent almost all the content of these metals in the sample.

The effect of pH on sensitivity has been already investigated by Weinzierl and Umland (1982). We confirm their results, and find pH 8.7 optimum rather than pH 9.2 as recommended by Mart and dimethylglyoxime (all dissolved and analysed in Milli-Q water) the contributions to the nickel and cobalt peaks in the voltammogram were near the limits of detection (0.011 µg L⁻¹ and 0.002 µg L⁻¹ respectively). These blank levels were established by sequential pH 9.2 as recommended by Mart et al. (1983).

For all reagents, such as Suprapur ammonia solution and dimethylglyoxime (all dissolved and analysed in Milli-Q water) the contributions to the nickel and cobalt peaks in the voltammogram were near the limits of detection (0.011 µg L⁻¹ and 0.002 µg L⁻¹ respectively). These blank levels were established by sequential additions of reagents and the observation of changes in the voltogram. They are susceptible to further reduction and this is in progress.

The reproducibility of analysis at concentrations of 0.2 µg L⁻¹ and 0.05 µg L⁻¹ of nickel and cobalt measured simultaneously was ±8% for nickel and ±2% for cobalt. If the elements were analysed separately, the figures improved to ±5% and ±1% respectively. These figures represent also the respective variability of the spike figures around the calibration line.

At higher levels (0.4 µg L⁻¹ for Ni and 0.4-0.06 µg L⁻¹ for Co) the reproducibility improved to about ±1% and ±0.5% respectively.

For added nickel and cobalt, the results obtained corresponded to the added amounts to within the reproducibility figures quoted, suggesting the accuracy is not worse. This shows the method should be adequate at the levels expected for seawater.

RESULTS AND DISCUSSION

At the ET-R2 station, as shown in Fig. 5, nickel in the surface water was about 0.25 µg L⁻¹. It decreased to about 0.11 µg L⁻¹ at 700 m and returned to 0.25 µg L⁻¹ at 2000 m (near the bottom).

In the case of cobalt, the level in surface water was about 0.015 µg L⁻¹, which decreased to about half at 700 m and continued to decrease slightly to about 0.003 µg L⁻¹ (near our limit of detection) at 2000 m. In contrast (Fig. 7), the vertical salinity distribution was uniform and showed no sharp gradients, except that there was a slight increase from the surface to 75 m. The Rhone mouth is fairly near this station and supplies a great deal of water to the Mediterranean but its influence on salinity at this station was practically nil. The variation of the nickel and cobalt (which as shown in Figure 5 vary much more than the salinity) must therefore be due to other causes.

For station GY-W the salinity profile (Fig. 7) is quite different from that of ET-R2. The salinity for the first four points is significantly less, then at about 200 m depth there is a sudden increase in salinity to values close to those observed for almost all the points at station ET-R2. One would have expected this for profile ET-R2. This minor anomaly could be related to the profiles observed for trace metal concentration.

The vertical distributions of nickel and cobalt in the water column of station GY-W presented in Figure 6 were also different to those at the ET-R2 station. The nickel in surface water was only 0.19 µg L⁻¹ (lower than the 0.25 µg L⁻¹ of ET-R2). A maximum was observed at 150 m with a decrease at 400 m back to about 0.2 µg L⁻¹ and little change thereafter. The distribution of cobalt in the same profile was rather similar but the maximum was somewhat less prominent. This maximum corresponds to the region in the salinity profile where the maximum change is occurring.

One explanation could be the presence of excess suspended matter at the depth where the salinity is changing which could affect the dissolved nickel and cobalt levels, but since we do not have figures for the amount of suspended matter at various depths the explanation must remain uncertain.

The vertical distribution of nickel did not entirely resemble that described for the Pacific by Bruland (1980) and Bruland et al. (1979) and Boyle and Huested (1983). In their case and with a much more uniform salinity profile than ours, nickel values increased steadily from the surface to reach a constant value with depth. Essentially the same was observed by Prange et
application of the equations used for example by lower than in the Pacific and argued on modelling land and Franks (1983) which demand a dangerous tenfold extrapolation, leads one to expect extremely unless the precision of analysis was exceptional. Direct GY-W.

That is not seen for station ET-R2, where there is an increase towards the bottom; however for station GY-W, if we disregard the aberrant points associated with the sudden change in salinity, the form of the distribution would follow the above authors quite closely. The Pacific values are double ours but the Atlantic values are very similar.

The increases towards the bottom for station ET-R2 cannot be easily explained, though similar increases are known for other elements such as copper (Boyle, Huested, 1983). What is most likely is that we are seeing the effects of winter mixing of water. Murray and Fukai (1978) describe a $^{137}$Cs profile, which is very unusual in that the amount of the isotope increases steadily towards the bottom of the sea. This was found near our sampling point ET-R2.

The profiles observed for cobalt, which show a reasonably steady decrease towards the bottom, are quite similar to those observed by Knauer et al. (1982).

Nutrient analyses at the sampling sites and for profiles were not directly available to compare with our profiles. The only data were from other expeditions in the Mediterranean. At the sites nearest to ours, their surface values were $120 \text{ ng L}^{-1}$, whereas we found 200 ng L$^{-1}$ for our point nearest to the surface. The discrepancy is probably not very great.

Indeed Spivack et al. (1983) comment that nickel, at least for surface waters just outside the Straits of Gibraltar, has concentrations lower than for almost all in the Mediterranean. At the sites nearest to ours, their surface values were 210 ng L$^{-1}$, essentially identical to our values. They also comment that the distribution of silicate differs from that for the metals. Immediately inside the Strait of Gibraltar, the concentration drops by a factor of three.

Although the nearest point of Kremling and Petersen (1981) to our sampling stations is 350 nautical miles away, the form of the silicate and phosphate profiles there is similar to the form of the nickel profile in our station ET-R2. Thus, for example, the phosphate rises from lower surface values to almost constant values at depth.

One factor possibly influencing the results in the Mediterranean is the precipitation of considerable wind-blown material from the Sahara, by winds such as the Sirocco. The effect of industrialization around this semi-enclosed sea is also not clear.

In the Table is given a list of recent work in which nickel and cobalt have been analysed under conditions which have followed to some extent the suggestions for contamination-free analysis laid down by Patterson and Settle (1976) and Zief and Mitchell (1976). The nickel level is found to be usually less than 0.3 $\mu$g L$^{-1}$ and the cobalt level less than 0.02 $\mu$g L$^{-1}$. Our figures are closely in accord with these.
CONCLUSION

Differential pulse cathodic stripping voltammetry has been relatively little used for nickel and cobalt analysis, but seems quite adequate. We do not find our results to differ from those obtained using other techniques as found by Wong et al. (1983).

We find limits of detection of 0.005 and 0.002 µg L⁻¹ and reproducibility not worse than ±8% and ±2% for nickel and cobalt respectively. There is minimum preparation of samples and the technique constitutes an excellent method for the aquatic environment or more specialized applications such as the measurement of ultra-trace cobalt in reactor coolant circuits.

Our results appear to reflect those typical of other oceans, especially the Atlantic, where nutrient conditions are nearer to ours, but are among the few to have been produced for the Mediterranean. This is particularly true for cobalt.

REFERENCES


If allowance is made for the sharp salinity change at one of our sampling stations, our profiles for these two elements are reasonably consistent with those found elsewhere, but a discrepancy possibly related to the winter mixing phenomenon in the area remains to be further investigated.

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