THE COLLECTORLESS FLOTATION OF SPHALERITE

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(ABSTRACT)

The flotation of sphalerite has been demonstrated without the use of collectors. The effect of redox potential, pH, and copper-activation have been investigated in tests using samples of pure mineral. It has been found that in general, collectorless flotation of sphalerite can be accomplished at potentials greater than -200 mV, SHE, and is more readily carried out in acidic solutions. It has also been shown that although copper-activation was necessary to achieve flotation recoveries above 35%, an excessive addition of cupric ions may result in a decrease in floatability.

Batch flotation experiments conducted using Elmwood Mine sphalerite ore have shown that in addition to copper-activation, the addition of sodium sulfide was required to obtain high grades and recoveries. If the ratio of the addition of these reagents is maintained such that the atomic ratio of cupric ions to sulfide ions is 0.31, good flotation is observed over a range of reagent dosages.

X-ray photoelectron spectroscopy (XPS) was conducted on pure mineral samples after microflotation testing. Based on the sulfur species identified on highly flotable samples, possible mechanisms for collectorless flotation of sphalerite have been suggested. These include: i) elemental sulfur formed under oxidizing conditions is responsible for collectorless flotation; ii) polysulfides or

metal-deficient sulfides formed as a result of mineral oxidation are responsible for collectorless flotation; and iii) removal of HS^- ions, which may render the surface hydrophilic, under oxidizing conditions. The third mechanism is based on the assumption that clean, unoxidized sphalerite surfaces are naturally hydrophobic. Evidence has been presented to suggest that the first mechanism may be responsible for collectorless flotation in acidic solutions, while the second mechanism may be of greater importance in nearly neutral or basic solutions where elemental sulfur is thermodynamically less stable.

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INTRODUCTION

GENERAL

The process of froth flotation is of extreme importance to the mineral processing industry. Over 2 x 10^9 tons of ore are processed using this technique annually (Leja, 1982).

This process relies on interfacial phenomena. The chemical environment is therefore extremely important in determining the interaction between the solid, liquid, and gas phases involved. The common method calls for particular surfactants, called collectors, to be adsorbed onto the solid surface, rendering it sufficiently hydrophobic to adhere to a rising stream of air bubbles.

As most minerals are naturally hydrophilic, the use of these collectors, as well as other reagents to promote collector adsorption is required. However, some minerals, such as graphite, sulfur and talc, do not require collector for their flotation (Gaudin, Miaw and Spedden, 1957). Most common sulfide minerals have long been thought to be hydrophilic and, have been treated as such in flotation practice.

However, some sulfides have been shown to float well without the addition of collector, suggesting that perhaps they are naturally hydrophobic. Another possible explanation for the observed collectorless flotation is that the chemical environment favors the formation of hydrophobic surface species which lead to good flotability.

This study attempts to examine the effect of pulp chemistry on the collectorless flotation of sphalerite, a zinc sulfide. The posssible

flotation mechanisms for collectorless flotation have been examined with a focus on identifying the hydrophobic species formed during flotation. The collectorless flotation process studied in the present work might lead to a savings in reagent costs and to increased efficiency.

LITERATURE REVIEW

There have long been questions about the specific character of sulfide minerals. Very early in the development of the science of mineral processing, it was noted that sulfide minerals had less affinity for water than the associated gangue minerals. The bulk oil flotation technique exploited this difference by inducing the sulfide minerals into an oil phase in the presence of water (Haynes,1860 and Everson,1886). This technique was soon abandoned due to the high consumption of oil.

Another early process that made use of the wettability characteristics of sulfides was known as the skin flotation technique (Bradford,1885). In this method of separation fine ore powder was slowly introduced onto the surface of a quiescent water bath. The sulfide minerals floated on the water and the gangue, which was easily wetted, sank. These early processes became obsolete when the use of a rising stream of air bubbles to buoy oil-coated sulfide minerals to the pulp surface was developed (Ballot, Sulman, and Picard, 1905).

Strong evidence has been presented both for and against the natural flotability of sulfide minerals. Sulman (1930) reported that galena and chalcopyrite were flotable without collectors. Other investigators, such as Ravitz and Porter (1933), Ravitz (1940), and Herd and Ure (1941) specifically suggested that galena was naturally flotable, if cleaned of all oxidation products. Ravitz and Porter (1933) further suggested that the role of xanthate, the most common sulfide mineral collector, was to chemically clean the mineral surface, thus revealing its inherent

flotability.

Contradictory evidence was presented, however, by Hagihara (1952) who used the electron diffraction technique to show that xanthate did indeed adsorb on galena surfaces. Sutherland and Wark (1955) demonstrated that different xanthates produced different contact angles on the same sulfide mineral surfaces. These facts seem to overwhelmingly refute Ravitz and Porter's conjecture.

The natural flotability of sulfides was challenged in work done by Knoll and Baker (1941). They showed that clean galena did not float without collector, nor did it adsorb xanthate. Another study where sodium sulfide (Na_2S) was used in an attempt to produce a clean galena surface indicated a need for collector (Wark,1938). In addition the depressant effect of Na_2S was noted. Gaudin (1932) discovered that this effect was true for both the reducing agent, Na_2S, and the oxidizing agent, potassium permanganate ($KMnO_4$) in a pure chalcopyrite system. This controversy was temporarily laid to rest by Taggart, del Giuduce, and Ziehl (1934) who speculated that the samples had been contaminated by oily substances or that the frothers had collecting properties themselves. Others (Plaksin, 1959; Glembotskii, Klassen, and Plaksin, 1963) have suggested that natural hydrophobicity is a result of the adsorption of molecular oxygen. The speculation was that this adsorption led to dehydration of the mineral surface allowing air to displace water more readily at the surface.

Collectorless flotation has gained renewed interest in recent years. Boyce, Venter, and Adam (1970) reported that it was being

applied for galena and sphalerite recovery at the Tsumeb concentrator in South Africa. Lepetic (1974) showed that chalcopyrite was flotable using only a frother after dry, autogenous grinding. Pyrrhotite has also been reported to be naturally flotable (Hodgson and Agar, 1984). In addition, Rey and Formanek (1960), Mino (1957), and Plaksin, Khazinskaya, and Tyurnikova (1955) have observed flotability of sphalerite without collector.

Heyes and Trahar (1977) discovered that the flotability of chalcopyrite depended on the potential of the pulp. They also took precautions to eliminate possible contamination by organics. They showed, by using alkaline salts to promote frothing, that organic frothers were not responsible for the phenomenon of collectorless flotation. Gardner and Woods (1979) confirmed Heyes and Trahar's results using electrochemical techniques. Using potential sweep voltammetry, they identified the presence of elemental sulfur as one of the oxidation products in alkaline pH. Since the mineral floated only under oxidizing conditions, where it can be oxidized to form elemental sulfur on its surface, these investigators considered the elemental sulfur to be the hydrophobic entity responsible for the collectorless flotation. One thing to note however, is that in addition to the elemental sulfur, they also identified the presence of iron hydroxide which is hydrophilic.

Finklestein, Allison, Lovell and Stewart (1975) differed with this view, finding no correlation between elemental sulfur on the mineral surface and natural flotability. Other work in this area has been done

by Clifford, Purdy, and Miller (1974), Trahar (1983), and others, who found evidence demonstrating a correlation between elemental sulfur and flotation. Heyes and Trahar (1984) have recently reported the importance of elemental sulfur in the collectorless flotation of pyrite and pyrrhotite.

Research done by Furstenau and Sabacky (1981) demonstrated that most sulfide minerals, including sphalerite, were naturally flotable when ground in an essentially oxygen-free environment. Their work supported that of other researchers (Rao, 1969; Gaudin, 1957; Rogers, 1962; Gaudin et al, 1959; Sutherland and Wark, 1955; Yonezawa, 1960) demonstrating that copper activation improved the flotation of sphalerite. Recent work (Perry, Tsao, and Taylor, 1984) has shown that copper activation produces a copper-sulfide compound on the mineral surface.

Other researchers have given alternative explanations for collectorless flotation. Yoon (1981) postulated that the use of sodium sulfide produced a sulfur-enriched mineral surface which was able to be floated. This theory has been supported by research done by Luttrell and Yoon (1982), Luttrell (1982), and Luttrell and Yoon (1984a) on chalcopyrite and sphalerite ores. In addition, Luttrell (1982) pointed out that there is an optimum ratio of copper activation to sodium sulfide addition yielding maximum recoveries for sphalerite flotation, verifying an earlier suggestion by Yoon (1981). He also reiterated the importance of potential in chalcopyrite flotation.

Luttrell and Yoon (1983b, 1984 a and b) indicate the presence of

polysulfides on the surface of highly flotable chalchopyrite. Their results indicate the presence of an intermediate oxidation state between sulfide ion, S^{2-} and elemental sulfur, S^{o}. This species, which can be inferred from their X-ray photoelectron spectroscopy (XPS) data, had previously been identified as the sulfur peak from covellite, Cu_2S, by Buckley and Woods (1981). Since the formation of polysulfides occurs at oxidizing potentials, the theory that they are responsible for flotation is consistent with results obtained earlier by Heyes and Trahar (1977), Gardner and Woods (1979) and, Trahar (1983). Hamilton and Woods (1983) have examined the mechanism for formation of the polysulfides. The assertion that the oxidation of the mineral to form polysulfide responsible for flotation has been recently supported by Hodgson and Agar (1984).

Hamilton and Woods (1984) and Buckley and Woods (1984) have offered a seemingly different explanation for this oxidation product. Instead of polysulfide being repsponsible for the collectorless flotation, they considered the metal-deficient mineral surface to be responsible for the flotation. They have suggested that this species, though thermodynamically unstable, would have a sulfur lattice structure very similar to that of the unoxidized mineral. By using electrochemical techniques, Hamilton and Woods (1984) were able to identify the potentials involved in the production of these metal-deficient sulfides and relate these potentials directly to the flotation behavior of several sulfide minerals.

SCOPE OF WORK

This investigation has included microflotation of pure sphalerite for the purpose of establishing the effect of redox potential, pH, and copper activation on its flotation behavior without collector. Batch flotation has been carried out on samples of Elmwood Mine sphalerite ore to determine the role of dissolved oxygen, redox potential, and sodium sulfide and copper sulfate additions. Further, an attempt has been made to determine if there exists an optimum ratio between Cu and S additions. In an effort to explain the mechanisms involved in the collectorless flotation of sphalerite, X-ray photoelectron spectroscopy (XPS) was used to examine the samples obtained from microflotation tests. From this data, possible mechanisms for the collectorless flotation of sphalerite have been suggested.

EXPERIMENTAL

MATERIALS

Ore Samples

The ore samples used for this study were obtained from the Jersey Miniere Elmwood mine in Carthage, Tennessee. The company shipped coarse run-of-mine ore which was crushed upon receipt to -28 mesh and split into 1000 gram lots. These were stored at or below -20 C to minimize surface oxidation. Prior to flotation testing, a bag of sample was removed from the freezer and split into two 500-gram lots, and ground in a ceramic ball mill. The average analysis of the feed ore used in this work was 15.2% Zinc.

Pure Minerals

The pure sphalerite sample used for microflotation tests was also from the Elmwood mine as obtained from Ward Scientific Company. Specimens were visually checked for contamination and impure samples were discarded. The pure specimens were then crushed with a mortar and pestle, and the -65 + 100 mesh fraction was obtained by hand screening. The crushed samples were then further examined visually for foreign materials and obvious surface discoloration. All particles that were of a questionable nature were removed with tweezers and discarded.

The -65+100 mesh sample, thus prepared, was placed in a vacuum dessicator and stored under vacuum until use. The pure mineral assayed 65.9% zinc by weight. The complete composition of the sphalerite as

determined by electron microprobe analysis is in table 1.

Reagents

Sodium sulfide flakes from Fisher Scientific were used as a surface cleaning agent in some batch flotation tests. These flakes were composed of 60 to 62% Na_2S, more than 35% water of crystallization, 1.5% sodium chloride and 2% unspecified sodium salts. For microflotation tests, where higher quality sodium sulfide was required, reagent grade sodium sulfide crystals ($Na_2S \cdot 9H_2O$), also from Fisher Scientific, were employed. These were carefully scraped and washed with doubly distilled water as recommended by Chen and Morris (1972) to remove surface oxidation products before weighing and dissolution. This high-grade sodium sulfide solution was used to make the pulp potential more reducing. Fresh solution was prepared daily. The certified A.C.S. grade potassium permanganate obtained from Fisher Scientific Company was used to adjust the pulp to more oxidizing conditions in some batch experiments.

When sphalerite activation was desired, certified A.C.S. grade cupric sulfate ($CuSO_4 \cdot 5H_2O$) from Fisher Scientific was used.

Dowfroth 250 from Dow Chemical Company was used as frother in all batch flotation experiments. A 1% solution of this frother was prepared to more accurately control the dosage. Lime, sodium hydroxide and hydrochloric acid were used to adjust pH. For some microflotation experiments, buffer solutions were prepared. The pH 4 buffer was made from 0.5M potassium biphalate. The pH 7 buffer made from sodium

Table 1. Summary of the composition of pure Elmwood sphalerite as determined by electron microprobe analysis.

ELEMENT	PER CENT BY WEIGHT
Zinc(Zn)	65.86
Sulfur(S)	32.62
Gallium(Ga)	0.61
Germanium(Ge)	0.49
Iron(Fe)	0.24
Cadmium(Cd)	0.18
Total	100.0

biphosphate (KH_2PO_4). A solution of 0.05M sodium borate, sodium carbonate, and sodium hydroxide was used to make a pH 10 buffer solution. These chemicals were obtained from various suppliers.

Compressed ultra-pure nitrogen from Airco Industrial Gases was used as the carrier gas for microflotation experiments.

All water used in preparing solutions and in microflotation tests was doubly distilled. A Corning Megapure system was used for second-stage distillation. Batch flotation experiments were conducted in tap water drawn from the Virginia Tech-Blacksburg, Virginia, water system.

EQUIPMENT

Electrodes and Meters

Potential Electrodes --The potential across a bright platinum-saturated calomel electrode pair was monitored during flotation experiments. A standard porous calomel electrode was used for all microflotation work. For batch flotation, a reverse-sleeve calomel reference electrode was used to provide improved response time and to lessen the possibility of clogging. The electrodes were refilled weekly with saturated potassium chloride solution.

A pin-type platinum electrode was used for the microflotation potential measurements. In batch flotation, a disc-type platinum electrode was used to increase the surface area presented for slurry contact and to facilitate proper cleaning. These electrodes were developed by Orion Research and supplied by Fisher Scientific.

The platinum-calomel pair was connected, along with the sulfide ion electrodes and the pH electrode, to a Fisher Accumet model 750 digital pH/millivolt meter through a Fisher model 753 electrode switching box. The output from this meter was recorded as a function of time using a Pedersen model 27MR strip-chart recorder.

Oxygen Probe --Dissolved oxygen was monitored in the batch flotation work using a Lazar Research Labs model DO-166 dissolved oxygen probe. This was connected to an Altex model 3500 digital millivoltmeter. The dissolved oxygen levels were recorded as a function of time using a Hewlett-Packard strip-chart recorder.

The membrane and reference solution of the oxygen probe were changed weekly and replaced with manufacturers standard equipment supplied by Cole-Parmer Equipment Company. The probe was zeroed in a 5% $NaSO_3$ solution and standardized to atmospheric conditions at the ambient temperature and pressure.

Sulfide Ion Electrode --In selected batch flotation tests, the sulfide ion concentration was monitored using an Orion Research silver/sulfide specific ion electrode coupled with an Orion Research double-junction reference electrode. The outer-chamber electrolyte of the reference electrode was changed daily and the inner-chamber electrolyte was changed weekly as suggested by the manufacturer.

This electrode pair was two-point calibrated using doubly distilled water as a blank and a sodium sulfide solution as a known concentration. The sulfide standard was prepared weekly and prevented from oxidizing using the SAOB II buffer described in the electrode instructions.

pH Electrode --Hydrogen ion concentration was monitored by use of an epoxy body, glass membrane pH electrode from Fisher Scientific. The electrode was calibrated in standard pH buffers obtained from American Scientific Products and Fisher Scientific. The electrode was cleaned between tests using 0.1 N HCl and rinsed thoroughly with doubly-distilled water.

Microflotation Apparatus

Microflotation was carried out in a set-up indentical to that used by Luttrell (1982). The diagram in figure 1 shows the arrangement. The pure mineral samples were floated in a Partridge and Smith type cell (1971) by sparging ultra-pure nitrogen through a medium porosity glass frit at the base of the cell. Gas flow was controlled and measured using a Gilmont micrometer capillary flowmeter. The particle suspension was gently stirred using a Teflon coated magnetic stir bar and a Sybron Nuova II magnetic stirrer.

Batch Flotation Apparatus

The automated laboratory flotation cell developed by Luttrell and Yoon (1983) was used for all batch flotation experiments. A diagram is included as figure 2. This apparatus required no modifications for this work.

X-ray Photoelectron Spectroscopy

The x-ray photoelectron spectroscopy (XPS) was done using an XSAM model 600 spectrophotometer manufactured by Kratos. The resolution limit of this machine was 0.46 eV. Additional information regarding this equipment may be obtained by contacting the manufacturer or the Polymer Lab, Department of Materials Engineering, Virginia Tech.

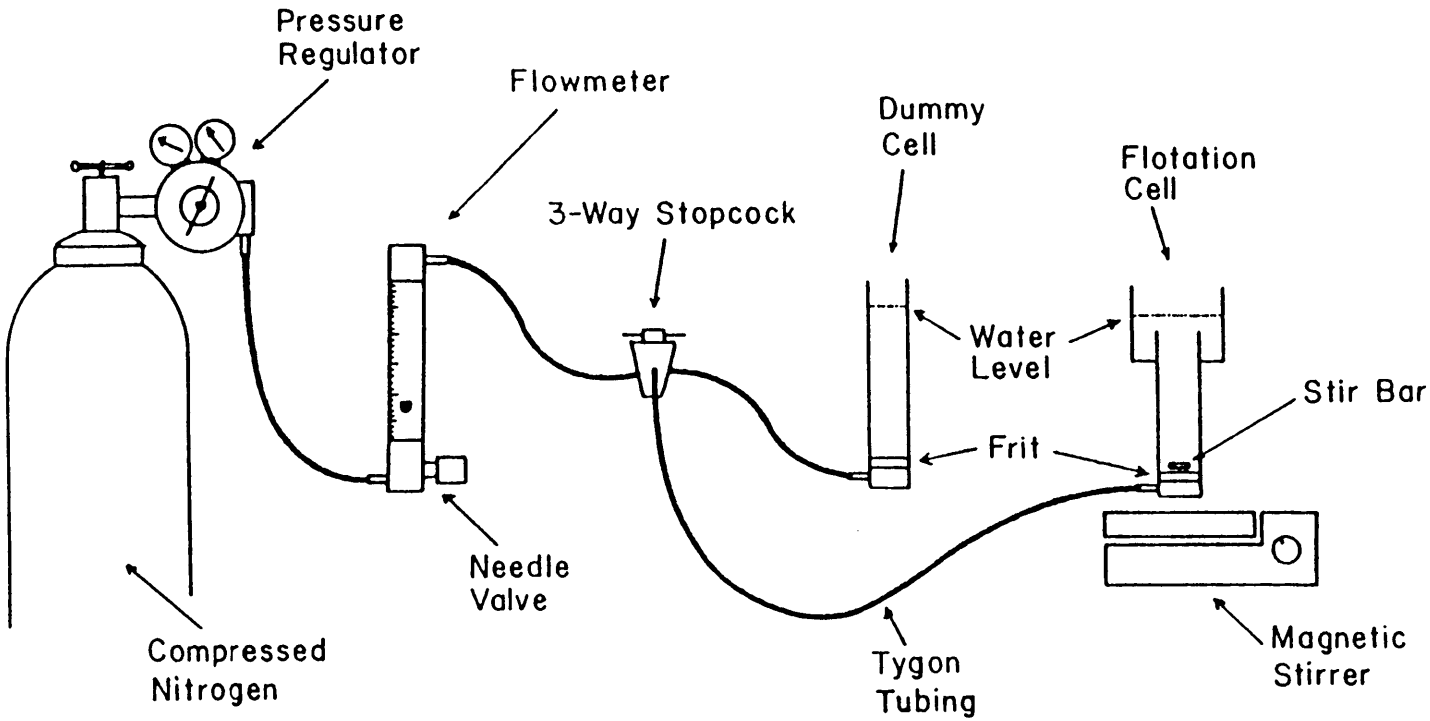


Figure 1. Schematic Diagram of the Microflotation Apparatus (Luttrell, 1982)

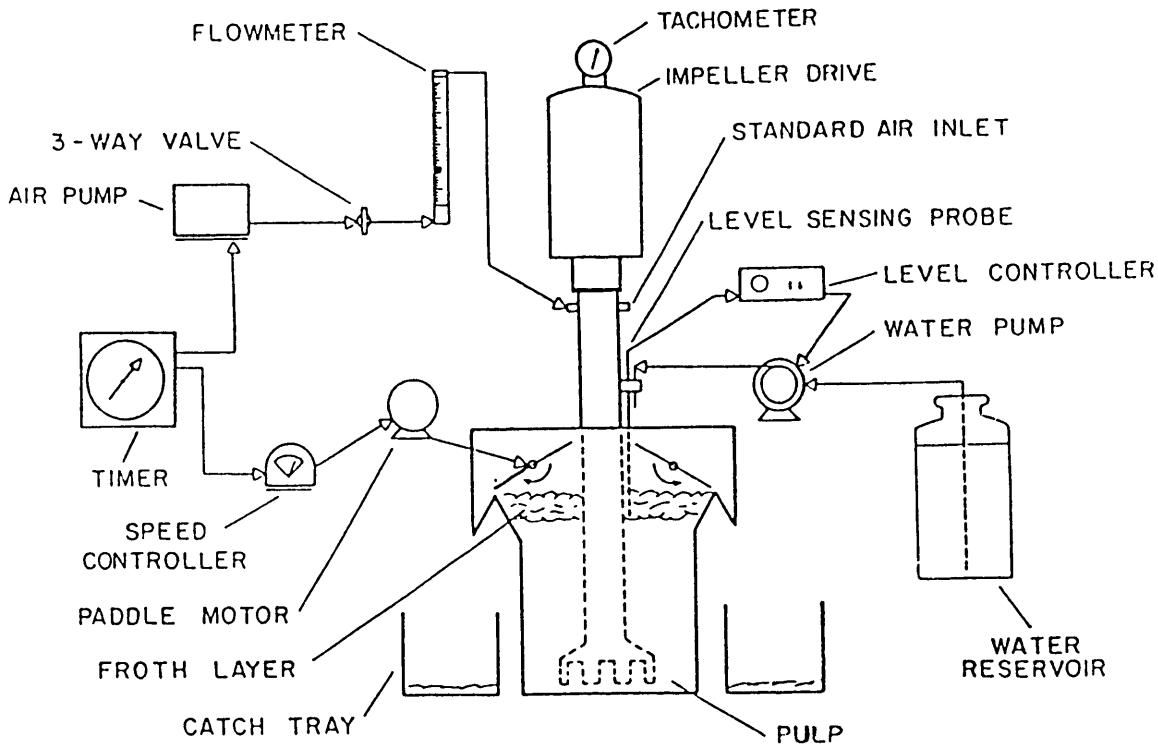


Figure 2. Schematic Diagram of the Batch Flotation Apparatus (Luttrell and Yoon, 1983a).

PROCEDURE

Measurement of Operating Variables

Potential --Potentials were measured by immersing a bright platinum-saturated calomel electrode pair into the suspension and reading a millivolt value from the voltmeter. This value was converted to the hydrogen scale by assuming the saturated calomel electrode had a potential of +0.242 volts, as determined by Bates (1964). This so-called "potential" is not intended to represent the reversible Nernst potential (Heyes and Trahar, 1977; Gardner and Woods, 1979). However, in general, positive potentials can be considered to be oxidizing and negative potentials, reducing.

The performance of the electrode pair was regularly checked using a ZoBell solution (Garrels and Christ, 1965). In addition, the surface of the platinum was mechanically cleaned with fine emery paper to ensure that any surface poisoning would be removed.

Dissolved Oxygen --The dissolved oxygen level was monitored by submerging the probe in the flotation pulp. The millivolt reading of the voltmeter was converted to dissolved oxygen content by a relationship where 0.1 volts equals 1 ppm oxygen. The probe was calibrated to atmospheric conditions and checked after each test.

Sulfide Ion --When sulfide ion concentration was measured, the specific ion- reference electrode pair was placed into the pulp

suspension. The meter was standardized to give the S level directly in ppm. This value was measured at the beginning of the experiment, at the onset of conditioning, at the beginning of flotation, and at the conclusion of the experiment in batch flotation tests.

pH --The pH was measured in an identical manner as were sulfide ion concentrations in batch flotation. In microflotation tests, pH was measured coincident with potential during conditioning.

Microflotation

The microflotation tests were carried out on pure sphalerite using the apparatus described earlier. In each test, 1.0 g of -65 +100 mesh particles was placed in an 150-ml beaker with approximately 70 ml of doubly distilled water. In the experiments conducted at constant pH, the buffers described earlier were used in place of doubly distilled water.

The potential measuring electrodes were placed in the suspension and the potential was adjusted to the desired level by reagent additions. Once the potential steadied at this level, the suspension was conditioned for 5 minutes. Except for those tests in which buffer solutions were used, no attempt was made to adjust the pH from the "natural pH" that resulted after reagent additions. After conditioning, the mixture was transferred to the flotation cell and flotation immediately begun. A one-minute flotation time was used. Forty ml/min ultra-pure nitrogen was passed through a glass frit for bubble

generation.

For tests where the sphalerite was desired to be copper-activated, the mineral sample was initially placed in a 250-ml Erlenmeyer flask with 50 ml $CuSO_4$ solution. This mixture was conditioned for 15 minutes utilizing a wrist-action shaker. After this time, the $CuSO_4$ was decanted off and the mineral was rinsed once with doubly-distilled H_2O. Then the sample was transferred to an 150-ml beaker, conditioned and floated as above. After flotation, both the floating and non-floating fractions were filtered, dried and weighed.

Batch Flotation

For batch flotation, approximately 500 g samples of the Elmwood ore, prepared as described earlier, were ground in a 10-inch ceramic ball mill with a 50% by volume (5 kg) charge of steel balls and 300 ml tap water. This pulp was transferred to the 2-liter plexiglas cell of the automated flotation machine. The necessary reagents were added, conditions adjusted, and conditioning begun. One minute prior to the starting of flotation, 1.5 ml of a 1% DF 250 solution (0.06 lb/ton) was added to the pulp.

At the appropriate time, the paddles of the machine were activated and the froth product collected for three minutes. This product was mixed with tap water to make up the volume of the cell, and floated to exhaustion as a cleaner stage.

The various pulp parameters were continuously monitored during conditioning and subsequent rougher flotation. In some tests, the level

of dissolved oxygen in the pulp was used to determine the starting point for flotation. In most tests, the pulp was conditioned six minutes after the addition of Na_2S and/or $CuSO_4$ dosages.

For the series of tests which were designed to verify the ratio of Cu^{2+} to S^{2-} necessary for good flotation, the procedure described by Luttrell (1982), was used. The sodium sulfide was added and the pulp conditioned for 10 minutes. The copper sulfate was then added and the pulp conditioned an additional 5 minutes before floating to exhaustion.

In this series of tests, the pH was controlled at 6.75 $\pm$ 0.1 by adding HCl as required. However, in the majority of batch tests, the pH was monitored but not controlled . A summary of reagent additions, pH, and other pertinent information for each test is included in Appendix A.

X-ray Photoelectron Spectroscopy

The samples for XPS analysis were prepared as for microflotation. More specifically, they were stirred in a beaker and reagents were added to bring potential to the desired level. Copper-activated specimens were in contact with 5×10^{-5} M $CuSO_4$ for 15 minutes, then mixed with doubly-distilled water prior to potential adjustment. The treatment of these samples is summarized in table 2.

The samples were then dried in a vacuum dessicator and stored under vacuum until just prior to running the spectra. The powdered sample was then mounted on double-stick tape and placed on the probe for insertion into the spectrophotometer. A wide-scan spectrum was then collected, followed by narrow scans for elements of interest, such as sulfur.

Table 2. Summary of preparation conditions for samples for XPS analysis.

Sample No.	Weight	Product	Flotability	Potential
1C	0.12g	Concentrate	11.65	+476mV
2T	1.03	Tailing	0.00	+829
3T	1.05	Tailing	0.00	-276
4T*	0.97	Tailing	4.90	+829
5C*	1.08	Concentrate	98.18	+517
6T*	1.04	Tailing	0.00	-458

*Copper-activated

EXPERIMENTAL RESULTS

MICROFLOTATION

The results of microflotation experiments were interpreted using flotability as the dependent variable. The outcomes were examined to determine the effect of potential, Cu^{2+} activation and pH. Flotability was defined as the percentage of the original 1-g sample of pure sphalerite collected in the head of the cell at the end of flotation. A summary of all experiments is included in Appendix B.

Effect of Potential

It was shown in this work that the flotation behavior of sphalerite is dependent on the potential of the solution prior to flotation. This agrees with the results obtained by other researchers for other sulfide mineral systems, such as Yoon and Luttrell (1984a) and Gardner and Woods (1979) for the chalcopyrite system.

Figure 3 shows these results for unactivated Elmwood sphalerite. This curve shows that flotation is negligible at potentials less than +200 mV, versus the standard hydrogen electrode (mv, SHE), and reaches a maximum of 35% at +432 mV. It drops off considerably at potentials greater than +600 mV. These results indicate that under certain potential conditions the surface of untreated sphalerite is at least partially hydrophobic.

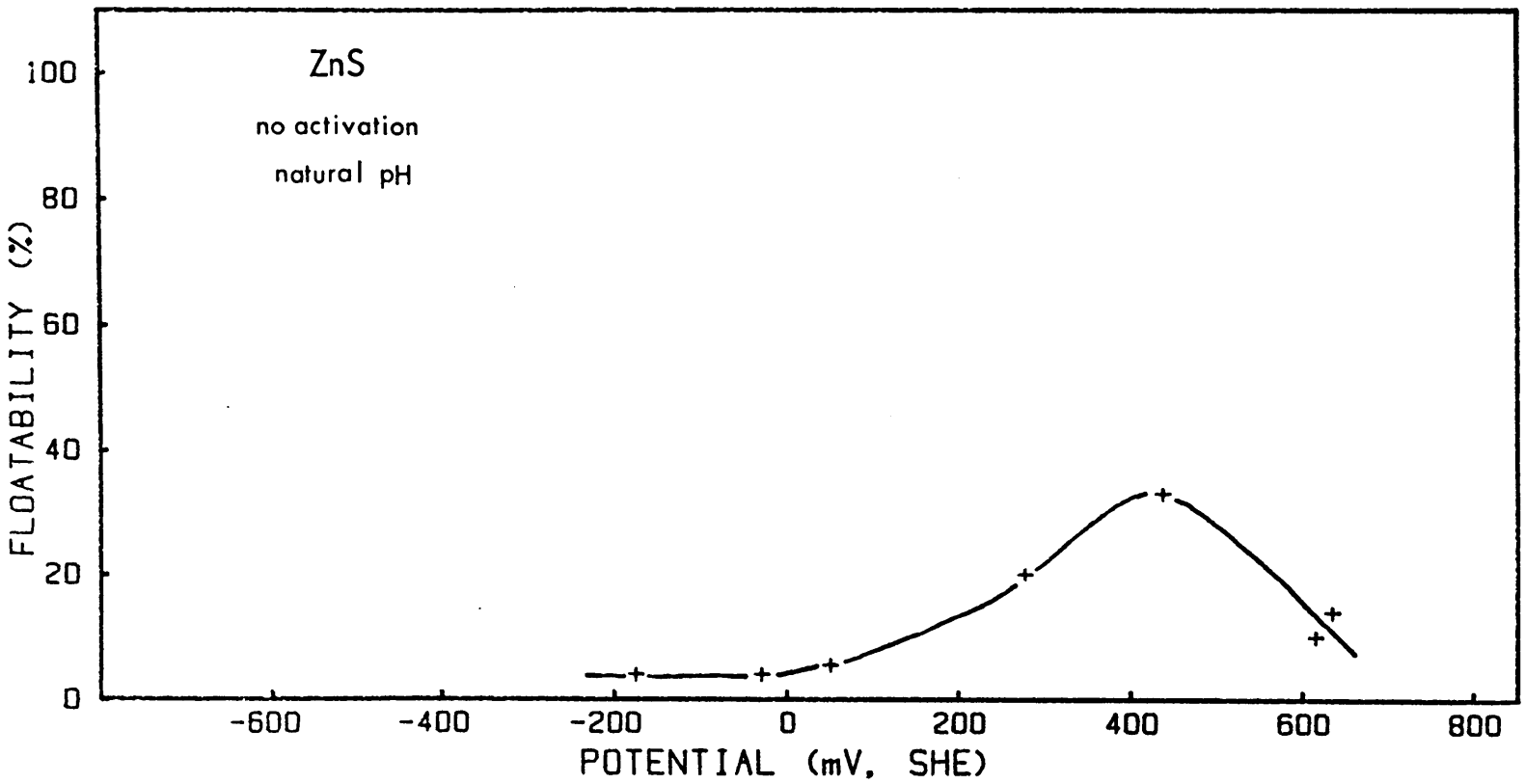


Figure 3. Flotation Behaviour of non-activated Elmwood Sphalerite.

Effect of Copper Activation

In view of the observations of Furstenau and Sabacky (1981) and others, an attempt was made to improve the flotability of the sphalerite by activating the surface with cupric sulfate ($CuSO_4 \cdot 5H_2O$). As was discussed in the procedure section, the mineral sample was treated with various concentrations of $CuSO_4$ solutions to provide this activation. The samples thus treated were conditioned at numerous potentials and then floated. The results in figure 4 show that the behavior of activated sphalerite is also dependent on potential. The concentrations of copper used in the activation step determined the exact flotation characteristics of the sphalerite.

At a copper sulfate concentration of 5×10^{-5} M, the range and amount of flotation was drastically improved from the non-activated case. Recovery of 33% of the sphalerite was obtained at potentials as low as 0 mV, SHE. The flotability was above 80% between +200 and +600 mV, reaching a maximum of 91% between +250 and +425 mV.

Increasing the copper sulfate concentration by one-hundred fold to 5×10^{-3} M increased the range of good flotability greatly. More than 40% of the sphalerite floated at potentials down to -300 mV. The flotability was greater than 80% in the potential range of -100 to +450 mV with a maximum of 97% around +150 mV. The recovery decreased rapidly for potentials greater than +450 mV, becoming less than 2% at +800 mV.

Further increase in copper concentration did not improve the flotation, however. At a copper sulfate concentration of 5×10^{-2} M, flotation behavior became complex. After an initial rise in flotability

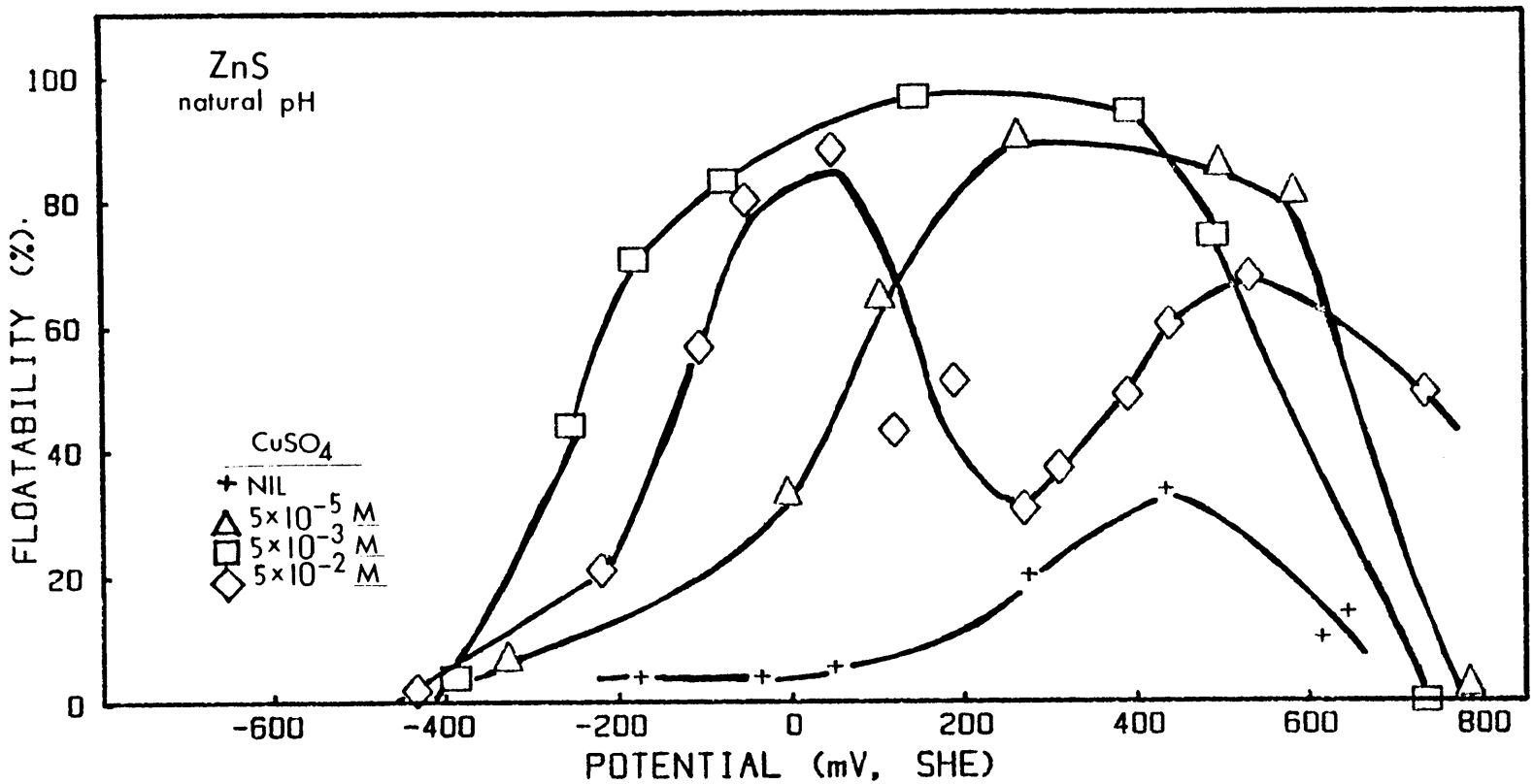


Figure 4. Effect of $CuSO_4$ dosage on ZnS flotability at natural pH. Na_2S or $KMnO_4$ added to adjust potential.

to a maximum of 88% at +50 mV, the recovery fell to 30% at +275 mV before rising to a second maximum of 67% at +535 mV. This bimodal response indicates that excess copper ions gave rise to two distinct flotation mechanisms, each having its own potential-dependent behavior.

Effect of pH

In the above tests, no attempt was made to control the solution pH. To examine the effect of this parameter on the hydrophobicity of pure sphalerite, microflotation experiments were carried out in pH 4, 7, and 10 buffer solutions. Both activated and non-activated series were conducted. The results of these experiments are shown in figure 5.

In both the activated and non-activated cases, the best results were obtained at pH 4. The non-activated sphalerite had a maximum flotability of 67% at approximately +200 mV at pH 4, compared with a 20% maximum for pH 7 and 7% for pH 10. Good flotability was exhibited for all potentials greater than 0 mV for pH4, with 25% of the sphalerite still floating at +1000 mV.

In the activated case, the flotability demonstrated even more variation with pH. At pH 4, the recovery was greater than 80% for all potentials between -100 and +900 mV, approaching 100% at potentials greater than 0 mV. Those tests conducted at pH 7 also showed flotabilities greater than 90% fo potentials between 0 and +700 mV. The recovery dropped drastically at potentials less than 0 mV and greater than +700 mV.

The experiments conducted at pH 10 showed a much narrower range of

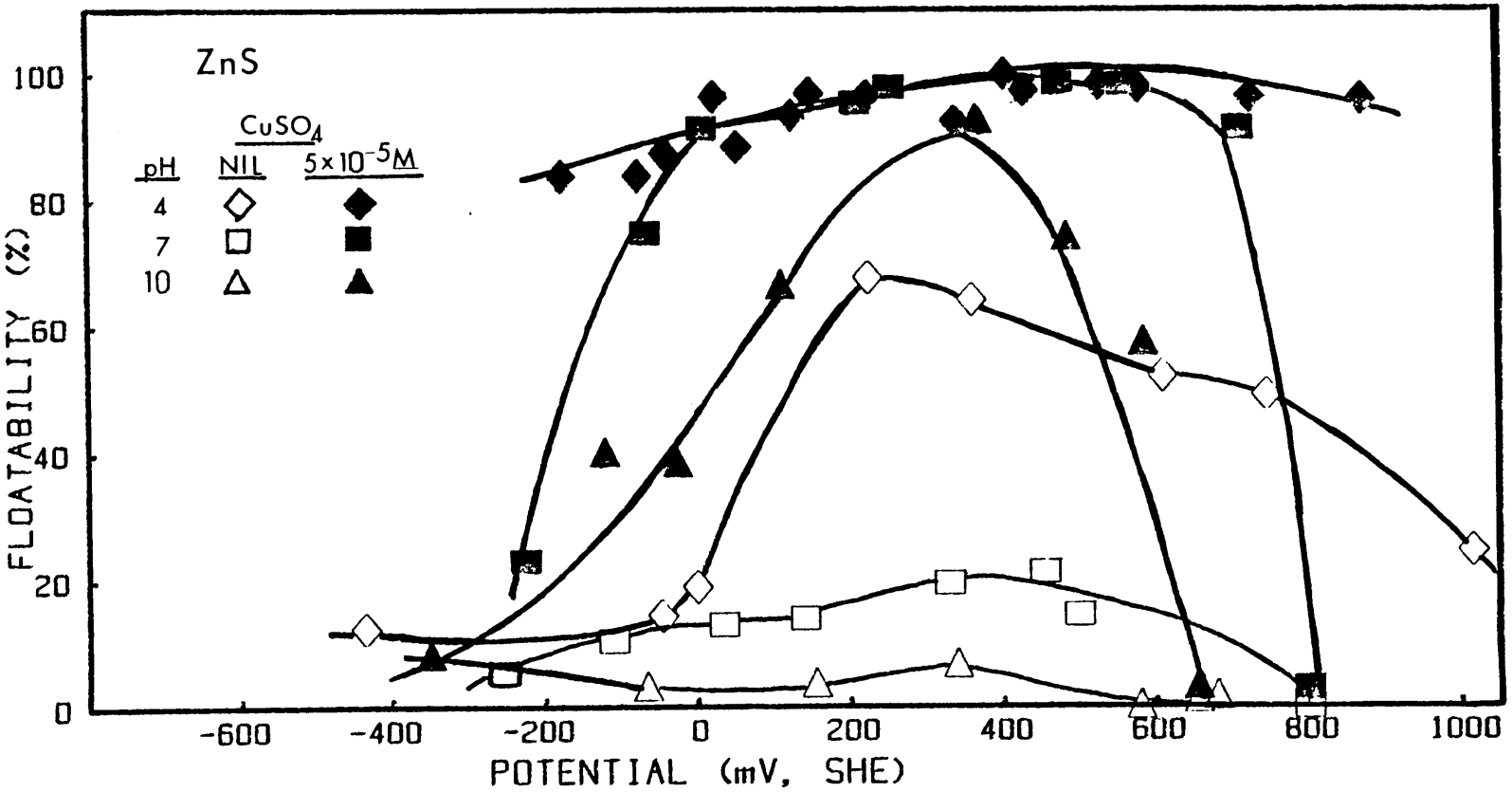


Figure 5. Effect of pH on the floatability of ZnS (non-activated and activated with 5×10^{-5} M $CuSO_4$). Na_2S or $KMnO_4$ added to adjust potential.

good flotability. They exhibited a slow increase in recovery from about 7% at -350 mV to a maximum of about 92% at +350 mV. The flotability decreased rapidly for potentials above the maximum point.

The limit for reducing potentials obtainable in pH 4 and 7 buffers was due to limitations in the chemical system. It was found that addition of Na_2S, in an effort to reduce the potential below the minimum values shown in figure 5, resulted in a marked increase in pH.

BATCH FLOTATION

Batch flotation experiments were conducted on 500-g lots of Elmwood mine sphalerite ore. Many pulp parameters, e.g. potential, dissolved oxygen, pH, and sulfide ion concentration, were monitored. Further, the effect of various reagent additions were examined. A complete summary of all batch experiments is in Appendix A.

Effect of Sodium Sulfide Dosage

Figure 6 illustrates the influence of Na_2S and $CuSO_4$ addition on flotation recovery of zinc from the Elmwood ore. It can be seen that any addition of Na_2S at $CuSO_4$ levels of less than 1 lb/ton, depressed the sphalerite flotation compared to tests where no sodium sulfide was added. At cupric sulfate dosages greater than 1 lb/ton however, the recovery increased if 0.25 lb/ton Na_2S were added. The grade of the flotation concentrate was high for all of these tests. Increasing the Na S dosage to 0.50 lb/ton brought a decrease in flotability. Additional tests conducted at a sodium sulfide addition of 1.5 lb/ton produced zinc recoveries of less than 2.5% at $CuSO_4$ dosages even up to 3.0 lb/ton, demonstrating that too much sodium sulfide is detrimental to flotation.

Effect of Cupric Sulfate Dosage

The effect of cupric sulfate activation on sphalerite recovery is also shown in figure 6. Flotation is enhanced greatly from nil at 0.0 lb/ton addition, to a maximum of 65 to 85% at dosages between 0.5 and

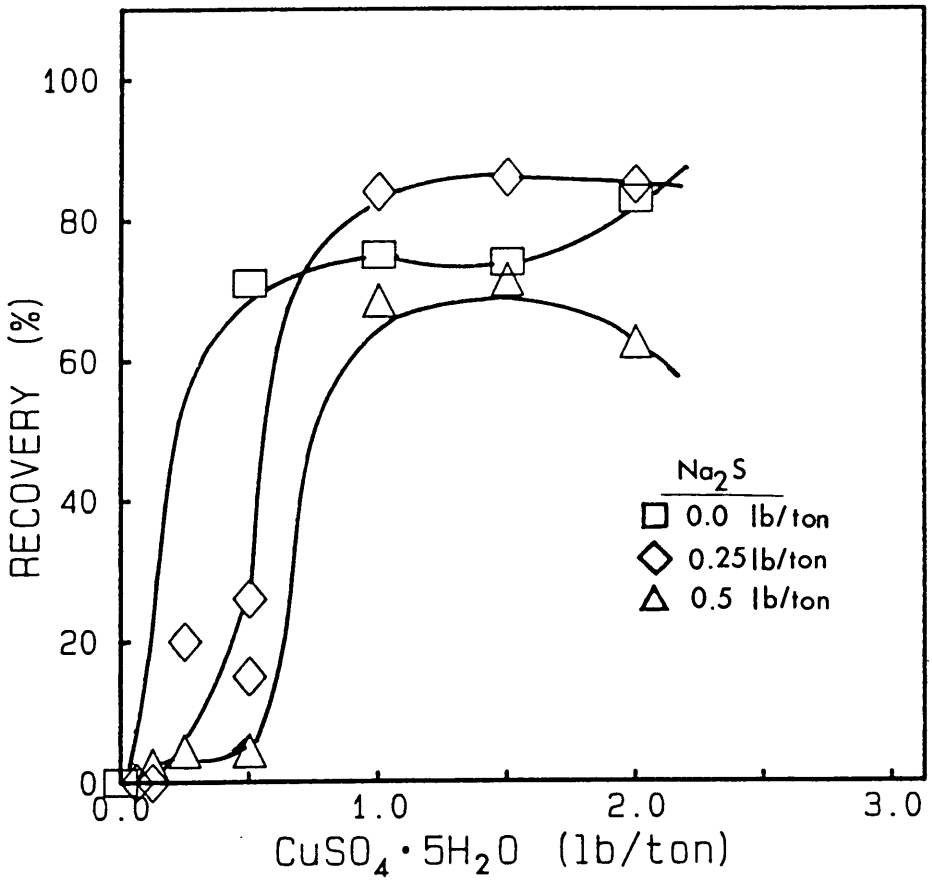


Figure 6. Effect of $CuSO_4$ dosage on recovery of Elmwood sphalerite at constant Na_2S addition.

2.0 lb/ton. This general behavior is observed for 0.0, 0.25, and 0.5 lb/ton additions of Na_2S. In the case of 0.5 lb/ton sodium sulfide addition, the recovery reaches a maximum at a 1.5 lb/ton dosage of $CuSO_4$, then falls markedly at 2.0 lb/ton.

Effect of Cupric Ion/Sulfide Ion Ratio

As the results in figure 6 indicate, there is a relationship between both copper sulfate and sodium sulfide additions and zinc recovery in the Elmwood sphalerite system. This relationship is more clearly demonstrated in figure 7. Using an identical technique as Luttrell (1982), results showing the most favorable ratio of added copper ions to added sulfide ions for optimum recovery were obtained. The maximum recovery was obtained at atomic ratios of 0.31. The recovery curves were identical for Na S additions of both 0.25 and 0.50 lb/ton. The grade curves showed a slight difference, however.

Effect of Dissolved Oxygen

To examine the importance of dissolved oxygen in collectorless flotation, several experiments were conducted in which various methods were used to bring the pulp oxygen concentration to a level of 9 ppm. This level was chosen by examining the dissolved oxygen level at flotation for a test in which good recovery was obtained for a high-grade sphalerite product, as can be seen in figure 8. A summary of the most significant of these tests conducted at 9 ppm is included in table 3. The recoveries and grades for cleaner flotation show little

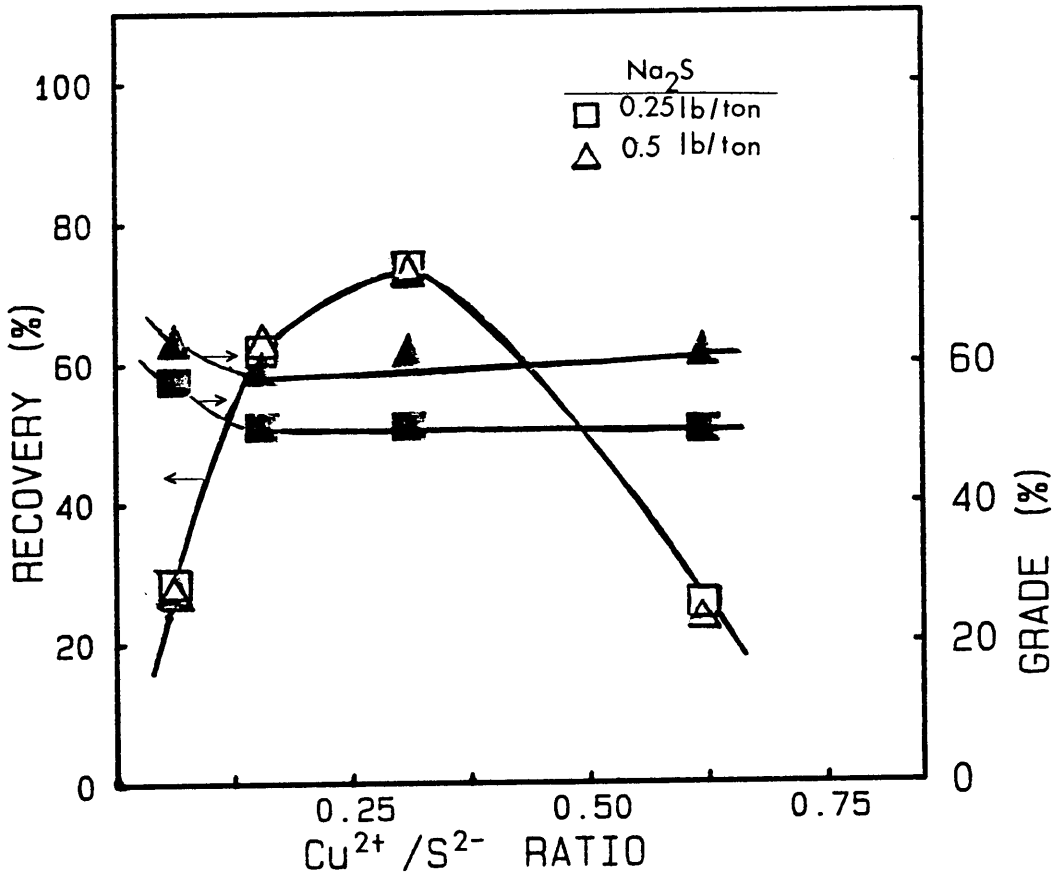


Figure 7. Effect of Cu^{2+}/S^{2-} ratio on recovery and grade of Elmwood sphalerite at pH 6.75.

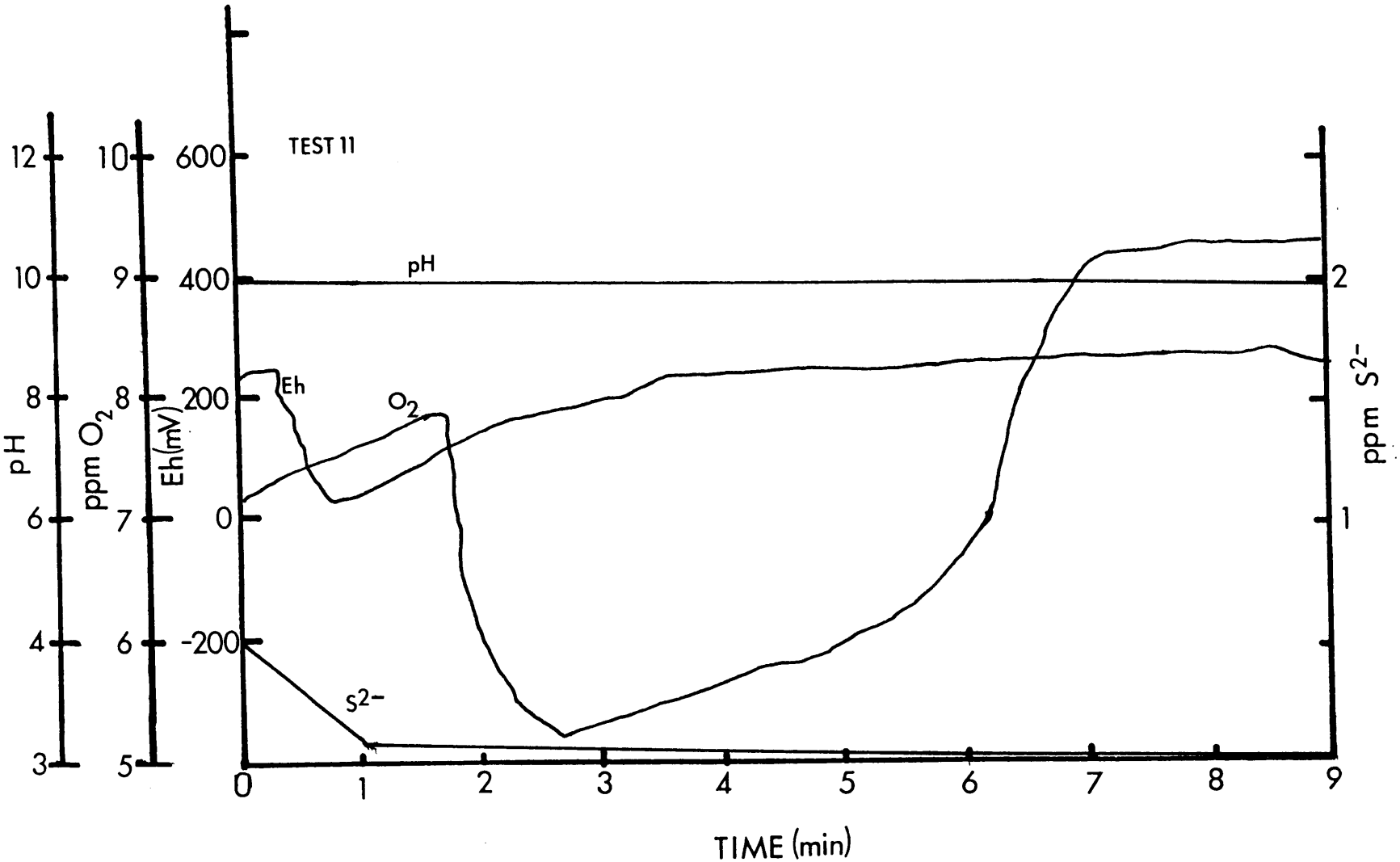


Figure 8. Record of operating variables for a test yielding high grade and recovery.

Table 3. Recovery and grade for flotation experiments conducted using 0.5 lb/ton Na_2S and 1.0 lb/ton $CuSO_4$ under different conditions.

Test	Conditions	Product	Grade	Recovery
11	Conditioned without air for 5 minutes	Rougher	37.46	75.66
		Cleaner	54.09	69.20
30	Conditioned without air until dissolved oxygen reached 9 ppm (12 min.)	Rougher	38.37	73.79
		Cleaner	57.83	67.96
31	Conditioned with air until dissolved oxygen reached 9 ppm (3 min.)	Rougher	49.18	73.56
		Cleaner	55.06	67.76
32	Conditioned without air 10 minutes, $KMnO_4$ added to bring dissolved oxygen to 9 ppm. (0.07g $KMnO_4$)	Rougher	42.29	90.57
		Cleaner	54.77	68.46

variation.

In test 32, the pulp was conditioned for 10 minutes and then 0.07 g of KMnO added. This produced an immediate increase in dissolved oxygen. The rougher concentrate in this test had a recovery of 90.57% at a grade of 42.29% Zn. This greatly exceeded the rougher recoveries obtained in the other tests and indicates the importance of dissolved oxygen, which is important in determining the pulp potential.

Effect of Permanganate Addition

In the series of tests conducted to examine the effect of potassium permanganate, the results indicate that there is an optimum level of permanganate addition. At a level of 0.2 lb/ton, the grade of the concentrate was 55.88% Zn at a recovery of 29.58%. When the dosage of KMnO was increased to 0.8 lb/ton, the grade decreased to 43.84% Zn, but the recovery was increased to 39.74%. Further increases in permanganate addition to 1.4 and 2.0 lb/ton gave very inferior results, with grades and recoveries indicating sphalerite depression.

Effect of Potential

As figure 8 and those in appendix D show, the pulp potential was monitored for all of the previously discussed batch flotation tests. The flotation data can be correlated to potential as well as the factors already examined by using this data. In general, the flotation of the ore was similar to that of the pure mineral observed in the microflotation tests. Specifically, the best flotation was obtained

when the pulp potential at the beginning of concentrate recovery was in the range of 0 to +600 mV SHE. Pulp potentials outside of this range greatly depressed the flotation of the sphalerite, although many other factors also affected the flotation behavior in a given test.

X-RAY PHOTOELECTRON SPECTROSCOPY

X-ray photoelectron spectroscopic (XPS) analysis was conducted on pure sphalerite samples after they had undergone microflotation testing. This surface analysis was done to identify the species that might have been responsible for flotation or the lack of flotation. In the cases where good flotability was observed, the microflotation concentrate was subjected to the analysis. In the other cases, the unfloated material was used. A standard of pure sulfur was also examined.

The raw spectra were deconvoluted using software developed by Kratos for use on their system. This provided detailed information regarding the oxidation states of sulfur present on the surface. Complete spectra and information for each sample is contained in appendix C. An example of raw and curve resolved Sulfur 2p spectra for sample 5C is included as figures 9 and 10.

Using accepted charge correction techniques, the binding energy of each peak was determined. This involved determining the binding energy of the carbon 1s peak and comparing it to the standard value of 284.9 eV. This difference was assumed to represent the shift in binding energies of all other peaks. When this shift was used to adjust the peak location of the curve-resolved S-2p peaks, the peaks could be

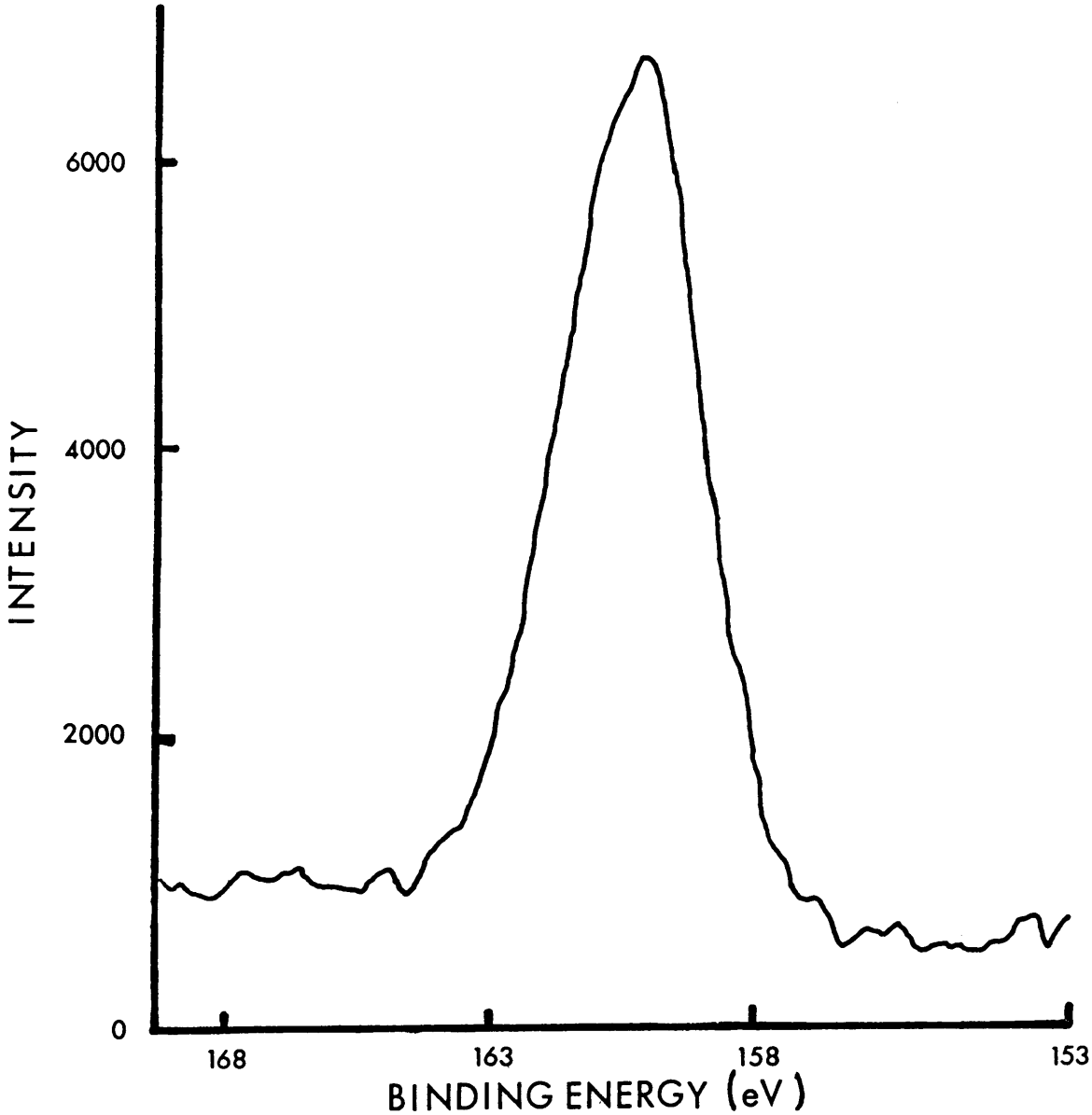


Figure 9. Raw Sulfur-2p spectra for sample 5C of pure sphalerite.

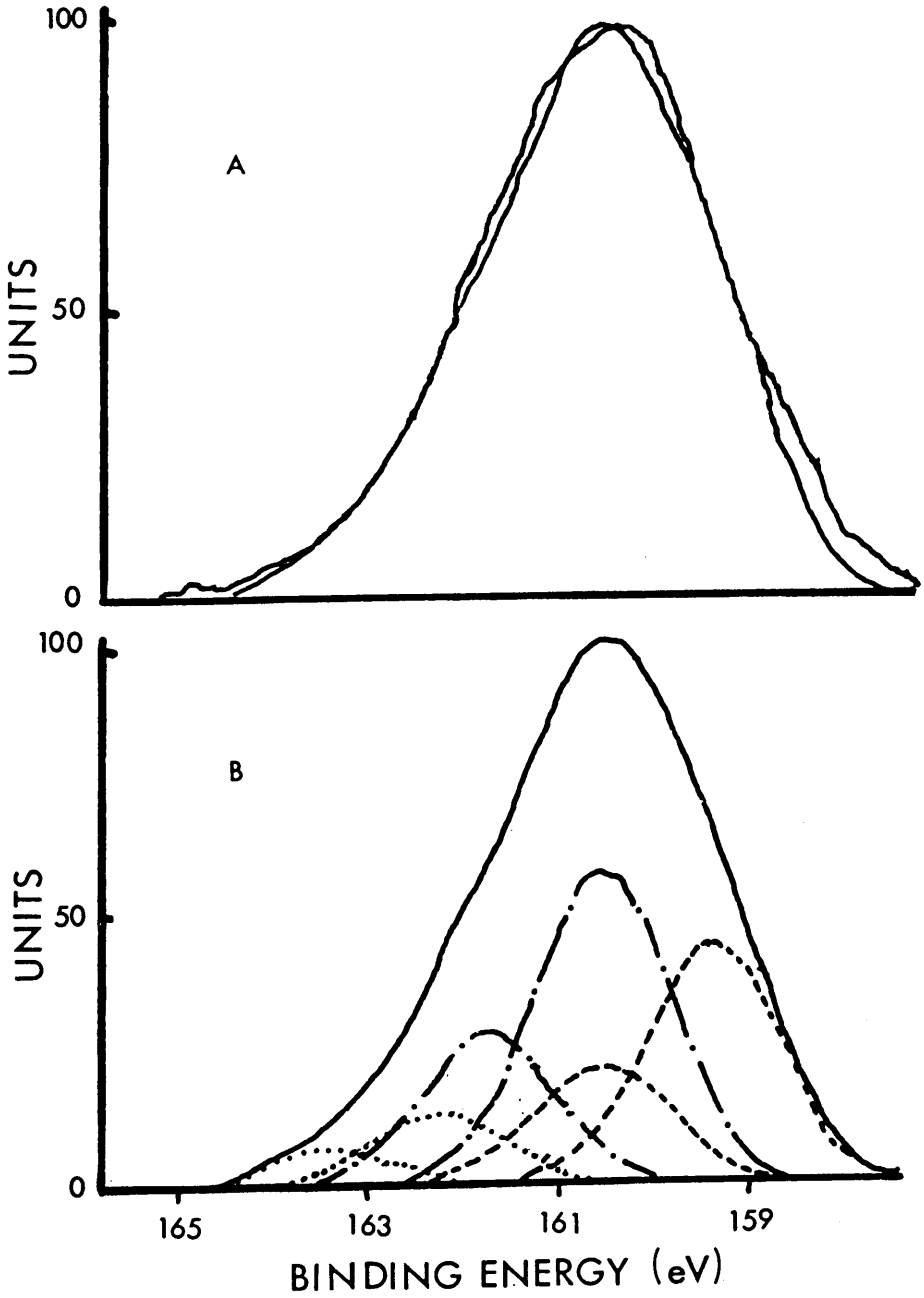


Figure 10. Sulfur-2p spectra for sample 5C of pure sphalerite. (A) Curve smoothed (B) Peak resolved. ····S°, -·-·S_x^{2-}, ---- S^{2-}.

compared to literature values for identification of the species present. Table 4 gives those peak identifications.

In addition, the ratio of peak areas of the different sulfur species gives a measure of the relative amounts of each on that sample surface. These relative abundances are included in table 5. As it can be seen, the samples that were treated at high oxidizing potentials (2T and 4T) have a lot of oxidized surface species such as S^o and other more oxidized hydrophillic species, such as $S_2O_3^{2-}$ and SO_4^{2-}, while samples 3T and 6T, which were treated at extremely reducing potentials, show a higher percentage of sulfur species in lower oxidation states. In addition, sample 5C, which alone showed good flotabilty, was the only sample to show the presence of S^- or S_x^{2-} on the surface. This seems to indicate a strong correlation of this species to flotability.

Table 4. Identification of surface sulfur species present on Elmwood sphalerite after various treatments as determined by XPS analysis.

Sample	Corrected Peaks S-2p1/2	S-2p3/2	Identification	Reference
Sulfur	163.3	162.1	S°	1,2
5C	163.3	162.1	S°	1
	161.6	160.4	S_x^{2-}	
	160.4	159.2	S^{2-}(w/ Cu)	3
1C	163.5	162.3	S°	
	162.4	161.2	S^{2-}(w/ Zn)	4
2T	164.2	163.0	SO_3^{2-}	5
	163.3	162.1	S°	
	162.0	160.8	S^{2-}(w/ Zn)	
4T	164.7	163.5	SO_3^{2-}	
	163.3	162.1	S°	
	160.9	159.7	S^{2-}(w/ Cu)	
3T	163.4	162.2	S°	
	162.4	161.2	S^{2-}	
6T	163.5	162.3	S°	
	162.4	161.2	S^{2-}	

References

1. Luttrell (1982)
2. Nordling (1972)
3. Langer, Helmer, and Weichert (1969)
4. Vesely and Langer (1971)
5. Hercules (1970)

Table 5. Relative surface abundance of various sulfur species present on Elmwood sphalerite after microflotation as determined by XPS analysis.

Sample	Copper Activ.	Abundance of Species (% of Total S on Surface) S^{2-}	S_x^{2-}	S°	SO_3^{2-}	Pot.	Flot.
5C	yes	38.52	49.53	11.95	-----	+517	98.18
1C	no	74.81	-----	25.19	-----	+476	11.65
2T	no	18.10	-----	54.60	27.30	+829	0.00
4T	yes	4.56	-----	67.92	27.52	+829	4.90
3T	no	71.61	-----	28.39	-----	-276	0.00
6T	yes	72.14	-----	27.86	-----	-458	0.00

DISCUSSION

FLOTATION

The results of microflotation experiments presented in previous sections demonstrate that pure sphalerite can be floated without use of collector, primarily at potentials above 0 mV, SHE. In order for this flotation behaviour to be significant, however, the sphalerite must be copper-activated. This activation, which can be represented by:

$$ZnS(s) + Cu^{2+}(aq) \longrightarrow CuS(s) + Zn^{2+}(aq)$$

(Sutherland and Wark, 1955), changes the potential range where collectorless flotation is possible as well. The critical potential for flotation onset can be lowered to below 0 mV by increasing the cupric sulfate dosage added.

The pH is also a factor in determining the potential range where collectorless flotation is possible (see figure 5). In addition, the pH greatly influences the maximum flotability obtained. A wider range of good flotability was obtained at pH 4 where nearly 100% flotability was observed at potentials between -100 and +900 mV for activated sphalerite. The potential range for maximum flotation at pH 10, on the other hand, was extremely narrow, with the point of maximum recovery of about 92% occuring at +350 mV. This behavior seems to agree with Luttrell and Yoon's (1984a) reasoning that pH may be important in forming hydrophobic surface species such as elemental sulfur or polysulfides, and is consistent with the findings of Clifford, Purdy and Miller (1974).

Similar trends in behavior were noted for batch flotation of Elmwood sphalerite ore. The ore also required copper-activation to float without collector. The ore also required the addition of Na_2S as well to obtain maximum recovery and grade. This upholds observations by Yoon (1981) and Luttrell and Yoon (1984).

The effect of Cu^{2+}/S^{2-} ratio was shown in figure 7. The ratio, previously noted by Luttrell (1982) as producing the best results at a value of 0.17, was found in this case to have a different point yielding optimum recovery, 0.31. This difference may be attributed to the difference in the characteristics of the ores used in these two studies. It is important to note that just as Luttrell found, the flotation behavior was independent of reagent dosages if this ratio were maintained. The findings of this work generally concur with those of Luttrell's work, and thus, his argument relating the cupric ion/sulfide ion ratio to the semi-conducting properties and the resulting flotability of the sphalerite surface is reinforced. That is to say that, because of the insulating nature of sphalerite (band gap 3.67 eV)(Teichman, 1964), copper-activation may be necessary to create a semi-conducting surface which can become involved in electrochemical oxidation reactions. Ralston, Alabaster, and Healy's (1980) work indicating that surface formation of elemental sulfur is closely related to the semi-conducting properties of the mineral seems to support this contention.

The results of the present study also support the findings of Gaudin (1932) indicating that in general sodium sulfide and potassium

permanganate act as depressing agents in flotation. The results presented here provide further support for the evidence presented by others that this is due to the effect these reagents have on pulp potential.

MECHANISMS

Induced Hydrophobicity by Oxidation

Elemental Sulfur --Metal sulfides have long been thought to be thermodynamically unstable in the presence of oxygen. Because of this instability, their surfaces are readily oxidized under the prevailing conditions of flotation circuits. Sphalerite behaves slightly differently since, unlike most metal sulfides, it is an insulator rather than a semi-conductor. This electronic property is changed, however, when the surface of the ZnS is copper-activated. Because it is believed that the copper ions replace the zinc in the sphalerite lattice during activation, the surface essentially becomes CuS. The surface, which would now be semi-conducting, would be more easily oxdized to form elemental sulfur.

The XPS spectra show the presence of S^o on all samples, regardless of the treatment conditions used. The amount of elemental sulfur on the surface (based on peak intensities and distribution of each species) varied from sample to sample. The samples treated at high oxidizing potentials showed the most sulfur as expected. Unexpectedly, however, the samples treated under reducing potentials had the next highest amounts. This was probably due to the oxidation of sulfide ions present in a film of sodium sulfide solution adhering to the mineral surface during the drying of the sample. The samples which exhibited the best flotability appeared to have the least amount of S^o on the surface.

The possibility that some sample oxidation took place during the drying prior to XPS analysis, raises doubts about the validity of the

interpretation of the data to explain flotation behavior. The samples which floated well without Na_2S added may provide more reliable information. Further, the presence and relative amounts of other sulfur-containing species agrees well with expected behavior at the treatment potentials.

The apparent lack of correlation between elemental sulfur on the surface and flotation behavior would seen to negate the importance of elemental sulfur as a flotation inducer. However, since the large quantity of S^o on the surface of the reduced samples (3T and 6T) can be explained by the oxidation of extraneous S^{2-} ions upon drying, and the lack of flotability of the oxidized samples (2T and 4T) by the presence of higher-oxidation-state, strongly hydrophillic sulfur species such as $S_2O_3^{2-}$, the assertion that the observed flotability of samples 5C and 1C is due to the presence of elemental sulfur, is a valid one. It is also consistent with the proposal of Gardner and Woods (1979) that elemental sulfur is responsible for collectorless flotation in the chalcopyrite system. Recent work by Heyes and Trahar (1984) has demonstrated that the collectorless flotation of pyrite and pyrrhotite is related to the production of elemental sulfur on the surface, lending further support to this proposal.

In addition, the results indicating that sphalerite floats better at acidic pH's is consistent with this theory. Many researchers have documented that the oxidation of sulfide minerals in acidic solutions results in the formation of elemental sulfur (Vizsolyi, Veltman, and Forward, 1963; Sato, 1966; Majima and Peters, 1966; Eadington and

Prosser, 1969; Bjorling, 1973). Thermodynamics also favors the increased stability of this elemental sulfur formed at pH's less than 7.5 (Garrels and Christ, 1965).

Polysulfides or Metal-Deficient Sulfides --As it can be seen in figure 10 and tables 3 and 4, the surface of sample 5C has a considerable amount of a sulfur species with a binding energy and oxidation state intermediate to S^{2-} and S^{o}. This species is best identifiable as a polysufide. Polysulfides can form as a result of the interaction of sulfur with an aqueous solution of sulfide (Chen and Morris, 1972) or by the aging or oxidation of sulfides or hydrosulfides in solution (Karchmer, 1970). Chen and Gupta (1973) have also demonstrated that when sulfur is produced in the presence of sulfide, polysulfides are immediately formed in some cases.

The pH of a system is of extreme importance in determining the stability of polysulfides. Chen and Morris (1972) and Chen and Gupta (1973) discovered that the concentration of polysulfides in a pH 8 solution is several times greater than that of elemental sulfur. The situation is reversed at pH 6 however. The concentration of polysulfides should increase with increasing alkalinity, according to the mass balance calculations done by Chen and Morris.

It has been demonstrated (Allen and Hickling, 1957) that polysulfides can adsorb on a metal surface through the following

$$S_x^{2-} + M \longrightarrow M{=}{=}{=}S_x$$

where S_x^{2-} represents the polysulfide and M the metal. Chen and Morris

(1972) showed evidence that the oxygenation of mildly alkaline sulfide solutions is 100 times greater in the presence of transition metals. It is very possible that transition metal sulfides could behave in much the same way. This metal-polysulfide complex would probably be hydrophobic since the bonding of the sulfur atoms in the polysulfide chain is very much like that in elemental sulfur.

Thus polysulfides may also play important roles in the oxidation and flotation of copper-activated sphalerite as well as other sulfides. They may also be important components of electrochemical reaction systems involving sulfide minerals. Similar electrochemical behavior has been suggested for both production of elemental sulfur and polysulfides on galena surfaces (Ho and Conway, 1978). This would seem to indicate that it is difficult to differentiate between the two processes electrochemically.

The sample 5C was prepared in distilled water with a pH presumably of around 7. This corresponds to the optimum pH for formation of polysulfides from a sulfide solution (Chen and Morris, 1972). Since sphalerite is one of the most soluble sulfides, in the absence of oxygen, (Yoon, 1981) it is concievable that enough S^{2-} ions are present to form these polysulfides.

Additional support is provided by the XPS data presented earlier (Table 3) which shows a peak at approximately 161.6 eV. This corresponds roughly to the peak assigned previously by Buckley and Woods (1981) and Luttrell (1982) as being Cu_2S. But as Luttrell points out, this peak could also be considered as an indication of the surface

presence of metal polysulfides. He suggests these may form by the reaction

$$2Cu^{+} + S_x^{2-} \longrightarrow Cu\text{-}S_x\text{-}Cu$$

where Cu^{+} represents the copper ions in the surface lattice and x represents the number of sulfur atoms in the polysulfide chain (usually 2-5). This is entirely possible since the formation of polysulfides from the CuS present on the surface would probably produce Cu^{+} ions on the surface by the reaction

$$XS^{2-} + YCu^{2+} \longrightarrow S_x^{2-} + YCu^{+} + (X-Y)e^{-}$$

where X and Y are probably equal to provide charge balance. Since the oxidation state of the sulfur in the middle of the polysulfide complex is nearly 0 and that on the end sulfur atoms is approximately -1, the XPS spectra may show these two peaks (Luttrell, 1982). The peaks at 161.6 and 163.3 eV for sample 5C correspond very closely to those indicated by Luttrell.

More recently, Hamilton and Woods (1983, 1984) and Buckley and Woods (1984) have attributed these intermediate peaks to the presence of a metal-deficient sulfide which they consider important to collectorless flotation. Their XPS data shows that the copper contained in this surface compound is present as copper (I), implying a formal oxidation state for the sulfur of -1/2, the same as is found in the polysulfide, S_4^{2-}.

From this data, an electronic structure of Cu_2S_4 was theorized for the metal-deficient sulfide found on the chalcopyrite. They also assumed that all of the sulfur atoms would have the -1/2 formal valence

state.

Other recent work (Perry, Tsao, and Taylor, 1984) suggests that the surface compound formed on copper-activated sphalerite is a copper (I) sulfide based on XPS and Auger parameter data. This compound, though identified as possibly being chalcocite (Cu_2S) could actually be a metal-deficient sulfide. Thus, the copper-activation of sphalerite at appropriate oxidizing potentials could produce a metal-deficient sulfide which would cause flotation behavior such as was found for sample 5C.

Since, in general, polysulfide and metal-deficient sulfide formation is enhanced at higher pH, it is possible that these species are responsible for collectorless flotation in alkaline or nearly neutral solutions. The flotation behavior observed in acidic solutions may be caused by elemental sulfur, on the other hand.

Inherent Hydrophobicity

The results of the microflotation tests conducted on pure and copper-activated sphalerite indicate that flotability decreases with increasing additions of sodium sulfide and thus with decreasing potential. To better understand the role that sodium sulfide addition plays in this system, it is important to consider the proportion of total sulfide present as S^{2-}, HS^-, or H_2S in aqueous solutions as a function of pH. Jones and Woodcock (1978) demonstrated that HS^- ions make up the greatest portion of the total sulfide at pH values between 7 and 13. Therefore, it might be considered that hydrosulfide ions are depressing the natural flotation of sphalerite and copper activated sphalerite under the reducing conditions.

HS^- ions have long been identified as depressants in xanthate flotation because of the competition of the hydrosulfide and xanthate ions for the mineral surface (Gaudin, 1957). Gardner and Woods (1979) and Trahar (1983) claimed that HS^- ions produce a reducing environment that prohibits the formation of elemental sulfur in collectorless flotation. Luttrell (1982) suggests alternatively that the adsorption of hydrosulfide ions on the mineral surface might render it hydrophilic. The S-H group can act as a proton donor and thus easily form hydrogen bonds (Vinogradov and Linnel, 1971) and, if the water molecules surrounding the mineral are proton acceptors, the adsorbed HS^- would give the mineral an hydrophilic character.

This argument implies that elemental sulfur may not be required for collectorless flotation. Failure to find a strong correlation between

elemental sulfur present on the mineral surface and flotability has been the case in much previous work (Finklestein et al, 1975; Heyes and Trahar, 1977; Pritzker, Yoon, and Dwight, 1980; Furstenau and Sabacky, 1981; and Luttrell, 1982). As was previously discussed, the present results cannot be easily interpreted using the elemental sulfur theory alone.

It has previously been indicated that the flotation response for both activated and non-activated sphalerite is best in acidic pH. If HS is responsible for hydrophilic depression of the mineral, this improved flotability may be due to the removal of HS^- from the system as H_2S gas. Of course, acidic conditions also favor the formation of elemental sulfur.

Under oxidizing conditions, the mineral may be depressed in a different way. At high oxidizing potentials, XPS shows large amounts of elemental sulfur, yet neither of these samples was flotable. This lack of flotability can be explained; at high oxidizing potentials, hydrophilic species such as CuO, $CuSO_4$, CuS_2O_3, and MnO_2 are readily formed as shown by XPS spectra. These species adversely affect the hydrophobic nature of the sphalerite surface.

The assertion that some species (e.g. HS^-, $CuSO_4$) is rendering the mineral surface hydrophilic is based on the assumption that clean sulfides are inherently hydrophobic. The increased flotability of copper-activated sphalerite could be explained on the basis that the CuS formed is less soluble than the ZnS (Yoon, 1981). The inherent flotability of sulfides is due to the inability of sulfide ions to form

H-bonds with the surrounding water molecules (Finkelstein et al, 1975; Furstenau and Sabacky, 1981). The weakness of this natural flotability theory is that sulfide minerals are extremely succeptible to oxidation. At even 1 x 10^{-10} M levels of dissolved oxygen, oxidation is likely to occur (Gaudin, 1972).

The present study has verified that collectorless flotation of sphalerite is related to the oxidation mechanism of the sphalerite or the CuS on the surface. Since oxidation of sulfide proceeds in an orderly progression from

$$S^{2-} \rightarrow S_x^{2-} \rightarrow S^- \rightarrow S^o \rightarrow S_2O_3^{2-} \rightarrow SO_3^{2-} \rightarrow SO_4^{2-},$$

the flotability of a mineral will be most influenced by the degree of oxidation of the mineral at the time of flotation. The results of the flotation experiments and the XPS experiments indicate that the chemical enviromment can cause this oxidative progression to be limited or to progress fully, producing the desired flotation behavior. In addition, these results favor the conclusion that polysulfides or metal-deficient sulfides are the species responsible for collectorless flotation of sphalerite in nearly neutral and slightly alkaline solutions. Elemental sulfur is probably responsible for flotation in acidic solutions, however.

SUMMARY AND CONCLUSIONS

The results of the present investigation may be summarized as follows:

1. Microflotation experiments conducted on non-activated and copper-activated samples of pure sphalerite in the absence of collector demonstrated that flotation was related to the potential of the chemical system. In general, better flotability was obtained in the range of potentials from 0 to +600 mV versus SHE.

2. The use of copper sulfate was essential in obtaining good flotation in both the microflotation and batch flotation tests. The concentration of the cupric sulfate used for activation was extremely important in determining the exact potential range where good flotability occurred.

3. In batch flotation tests conducted with Elmwood mine sphalerite ore, the use of both cupric sulfate and sodium sulfide was required to obtain maximum grade and recovery in collectorless flotation practice. Good flotability was obtained for a wide range of reagent additions as long as the atomic ratio of Cu^{2+}/S^{2-} was maintained at 0.31.

4. The atomic ratio of Cu^{2+}/S^{2-} required for optimum flotability of the Elmwood sphalerite differed from that obtained by earlier research on a different ore. This seems to indicate that the ratio may be a function of each particular ore.

5. The sphalerite recovery in batch flotation tests was found to improve in neutral to acidic solutions. The increased flotability was

postulated to be caused by the increased stability of S^o in acidic solution or to the removal of hydrophillic HS^- by protonization to H_2S gas.

6. The X-ray photoelectron spectroscopic analyses of the flotation products indicated the possibility of polysulfide ions or metal-deficient sulfides on the surface of a highly-flotable copper-activated sample. The chemical reactions necessary to produce this species could have taken place under the conditions of this test. This supports Luttrell and Yoon's work (1984b) as to the role of polysulfides in collectorless flotation.

7. Sodium sulfide and potassium permanganate were found in general to depress flotation. This may support the theory that sulfide surfaces are inherently hydrophobic. The depressant effect of Na_2S may be caused by the adsorption of HS^- which may hydrogen bond to surrounding water molecules. $KMnO_4$ may cause the formation of hydrophillic oxidation products, such as manganese dioxide, on the mineral surface.

8. Collectorless flotation of sphalerite may be viewed as being the result of superficial oxidation of the mineral surface. Insufficient or over oxidation can result in inferior flotation behavior. The use of specific reagents, such as potassium permanganate or sodium sulfide, can speed up or limit the oxidation.

INDUSTRIAL APPLICATION

The results of the present study have demonstrated that collectorless flotation of sphalerite is possible using only a frother after treatment with copper sulfate and sodium sulfide. Since the cost of sodium sulfide is substantially less that that of collectors used in industry today, the collectorless flotation of sphalerite may result in savings in operation costs. In addition, the need for pH regulators such as lime is eliminated in collectorless flotation.

The current economic crisis in the mining industry makes it essential that cost cutting measures be implemented. With the price of zinc at only 34.5 cents per pound, many mining companies have found it impossible to make a reasonable profit and have ceased to operate. More efficient and cost-effective methods of mining and beneficiation are required to rejeuvenate the industry.

In addition, the results of this work underscore the importance of the potential of the flotation pulp as a major variable in achieving good flotation behavior, as has been pointed out by other investigators (Luttrell and Yoon, 1984a; Heyes and Trahar, 1977; Walker, Stout, and Richardson, 1982). Industrial utilization of potential electrodes in flotation control may lead to more efficient metal processing and recovery.

RECOMMENDATIONS FOR FURTHER WORK

Based on the results of the present investigation, further study is recommended in the following areas:

1. The physical and chemical significance of the cupric ion/sulfide ion ratio should be investigated. Special attention should be paid to the crystal structure and electronic properties of the sphalerite that are important in determining this ratio.

2. Photo-conductivity and other semi-conducting properties of copper-activated sphalerite should be investigated and quantified.

3. Additional XPS studies should be conducted to determine the surface species present on sphalerite after treatment at various pH's and cupric sulfate concentrations.

4. Research to determine the collectorless flotation characteristics of covellite and chalcocite should be conducted and the results compared to those obtained for copper-activated sphalerite.

5. Analysis of the surface of highly-flotable sphalerite should be conducted whicle the mineral is still in the flotation pulp at the prevailing test conditions using a technique such as Fourier Transform Infrared Spectroscopy (FTIR). This would prevent the problems associated with the possible oxidation of the mineral surface as a result of the drying required prior to using analytical techniques such as XPS.

LITERATURE CITED

Allen, P.L. and Hickling, A., "Electorchemistry of Sulfur," Trans. Faraday Soc., 53, 1626-1635 (1957).

Ballot, Sulman, and Picard, British Patent No.7803 and U.S. Patent No. 835120 (1905).

Bates, R.G., Determination of pH, Wiley, New York, 458-483 (1964).

Bjorling, G. "Teaching of Mineral Sulfides by Selective Oxidation at Normal Pressure," 2nd Int. Symp. Hydrometallurgy, Chpt. 26, 701-717 (1973).

Boyce, J.R., Venter, W.J. and Adam, J., "Beneficiation Practice at the Tsumeb Concentrator," In: D.O. Raush and B.C. Mariacher (Editors), World Symp. on Min. and Met. of Lead and Zinc, AIME, New York, 542-570 (1970).

Bradford, H., "Method of Saving Floating Materials in Ore Separation," U.S. Patent No. 345951 (1885).

Buckley, A. and Woods, R., "Investigation of the Surface Oxidation of Sulfide Minerals Via Esca and Electrochemical Techniques" Engineering Foundation Conference on Interfacial Phenomenal in Mineral Processing, August 2-7, Rindge, New Hampshire (1981).

Buckley, A. and Woods, R., "An X-ray Photoelectron Spectroscopic Investigation of the Surface Oxidation of Sulfide Minerals," In P.E. Richardson, S. Srinivasan, and R. Woods (Editors) Proc. of the Int. Symp. on Electrochem. in Mineral Metal Processing, Proceedings vol. 84-10, The Electrochemical Society, Pennington, N.J., 286-302 (1984).

Chen K.Y. and Gupta, S.K. "Formation of Polysulfide in Aqueous Solution," Env. Letters, 4, 187 (1973).

Chen, K.Y. and Morris, J.C., "Kinetics of Oxidation of Aqueous Sulfide by O," Enviro. Sci. amd Tech., 6 (6), 529-537 (1972).

Clifford, R.K. and Miller, J.D., "Formation and Detection of Elemental Sulfur on the Surface of Sphalerite in Aqueous Sustems," AIME Annual

Meeting, Feb. 24-28, Dallas, Texas (1974).

Clifford, R.K., Purdy, K.L. and Miller, J.D., "Characterization of Sulfide Mineral Surfaces in Froth Flotation Systems Using Electron Spectroscopy for Chemical Analysis," AIChE Symp. Series No. 150, 71, 138-147 (1975).

Eadington, P. and Prosser, A.P., "Oxidation of Lead Sulfide in Aqueous Suspensions," Trans IMM, June C74-C82 (1969).

Everson, C.J., "Process of Concentrating Ores" U.S. Patent No. 348157 (1886).

Finklestein, N.P., Allison, S.A., Lovell, V.M. amd Stewart, B.V., "Natural and Induced Hydrophobicity in Sulfide Mineral Systems," In: P. Somasundaran and R. G. Grieves (Editors), Advances in Interfacial Applications to Flotation Research, AIChE, Symp. Ser. No. 150, 71, 165-175 (1975).

Furstenau, M.C. and Sebacky, B.J., "On the Natural Flotability of Sulfides," Int. J. Mineral Process., 8, 79-84 (1981).

Gardner, J.R. and Woods, R., "An Electrochemical Investigation of the Natural Flotability of Chalchopyrite," Int. J. Mineral Process., 6, 1-16 (1979).

Garrels, R.M. and Christ, C.L., Solutions, Minerals and Equilibria, Harper and Row, New York (1965).

Gaudin, A.M., Flotation, McGraw-Hill, New York, 2nd ed. 1957 (1932).

Gaudin, A.M., "The Role of Oxygen in Flotation," J. Coll. Interface Sci., 47, 309-314 (1972).

Gaudin, A.M., Furstenau, D.W., and Mao, G.W., Trans. AIME, 214, 430 (1959).

Gaudin, A.M., Miaw, H.L. and Spedden, H.R., "Native Flotability and Crystal Structure," Proc. 2nd Annual Congress of Surface Activity, Butterworth Sci., London, 3 (1957).

Glembotskii, V.A., Klassen, V.I., and Plaksin, I.N., Flotation, Primary Sources, New York (1963).

Hagihara, H., J. Phys. Chem., 56, 610-616 (1952).

Hamilton, I.C. and Woods, R., J. Appl. Electrochem., 13, 783-794 (1983).

Hamilton, I.C. and Woods, R., "A Voltammetric Study of the Surface Oxidation of Sulfide Minerals," In: P.E. Richardson, S. Srinivasan and R. Woods (Editors), Proc. of the Int. Symp. on Electrochem. in Mineral and Metal Process., Proc. vol. 84-10, ECS, Pennington, N.J., 259-285 (1984).

Haynes, W., British Patent No. 488, February 23 (1860).

Hercules, D.M., "Electron Spectroscopy," Anal. Chem., 42, 20-40A (1970).

Herd, H.H. and Ure, W., J Phys. Chem., 45, 93 (1941).

Heyes, G.W. and Trahar, W.J., "The Natural Flotability of Chalchopyrite,"Inst. J. of Min. Proc., 4, 317-344 (1977).

Heyes, G.W. and Trahar. W.J., "The Flotation of Pyrite and Pyrrhotite in the Absence of Conventional Collectors," In: P.E. Richardson, S. Srinivasan and R. Woods (Editors), Proc. of the Int. Symp. on Electrochem. in Min. and Metals Process., Proc. vol 84-10, ECS, Pennington, NJ, 219-232 (1984).

Ho, F.C. and Conway, B.E. "Electrochemical Behavior of the Surface of Lead Sulfide Crystals as Revealed by Potentiodynamic, Reflectance, and Rotating-Electrode Studies," J. Coll. and Interface Sci., 65 (1), 19-35 (1978).

Hodgson, M. and Agar, G.E., "An Electrochemical Investigation into the Natural Flotability of Pyrrhotite," In: P.E. Richardson, S Srinivasan and R. Woods (Editors), Proc. of the Int. Symp. on Electrochem. in Min. and Metals Process., Proc. vol 84-10, ECS, Pennington, NJ, 185-210 (1984).

Jones, M.H. and Woodcock, J,F., "Evaluation of Ion-Selective Electrode for Control of Sodium Sulfide Additions During Laboratory Flootation of Oxidized Ores," Trans. IMM, C99-C105 (1978).

Karchmer, J.H., The Analytical Chemistry of Sulfur and Its Compounds, Wiley-Interscience, New York, (1970).

Knoll, A.F. and Baker, D.B., AIME Tech. Pub. 1313, Mining Technology, May (1941).

Langer, D.W., Helmer, J.C. and Wiechert, N.H., "New Method for Determination of Impurity Levels with Respect to the Bonds of the Host Crystal (ZnS;Mn),"
J. Lumin., 1, 341-347 (1969).

Leja, J., Surface Chemistry of Froth Flotation, Plenum Press, New York, (1982).

Lepetic, V.M.," Flotation of Chalchopyrite Without Collector After Dry, Autogenous Grinding," C.I.M. Bulletin, June, 71-77 (1974).

Luttrell, G.H. "The Collectorless Flotation of Chalcopyrite and Sphalerite," MS Thesis, Virginia Polytechnic Institute and State University, (1982).

Luttrell, G.H. and Yoon R.H., "Automation of a Laboratory Flotation for Improved Performance," Int. J. Mon. Proc., 10, 165-172 (1983a).

Luttrell, G.H. and Yoon R.H., "Surface Chemistry of Collectorless Flotation of Chalcopyrite," AIME Annual Meeting, March 6-10, Atlanta, Georgia, (1983b).

Luttrell, G.H. and Yoon, R.H., "The Collectorless Flotation of Chalcopyrite Ores Using Sodium Sulfide," Int. J. Min. Proc., 13, 271-283 (1984a).

Luttrell, G.H. and Yoon, R.H., "Surface Studies of the Collectorless Flotation of Chalcopyrite," Colloids and Surfaces, 12, 239-254 (1984b).

Majima, H. and Peters, E., "Oxidation Rates of Sulfide Minerals by Aqueous Oxidation at Elevated Temperatures," Trans. AIME, 236, 1409-1413 (1966).

Mino, H., "Fundamental Studies on Sphalerite in Relation to Mineral Dressing," J. Min. Inst. Japan, 73, 93-102, 221-229 (1957).

Nordling, C., "ESCA: Electron Spectroscopy for Chemical Analysis," Angew. Chem. Int. Ed. Engl., 11, 83-92 (1972).

Partridge, A.C. and Smith, G.W., "Small Sample Flotation Testing: A New Cell," Trans. IMM, Sect. C, 80, C199-200 (1971).

Perry, D.L., Tsao, L. and Taylor, J.A., "Surface Studies of the Interaction of Copper Ions with Metal Sulfide Minerals," In: P.E. Richardson, S. Srinivasan, and R. Woods (Editors), Proc. of the Int. Symp. on Electrochem. in Mineral and Metal Process., Proc. vol. 84-10, ECS, Pennington, N.J., 169-184 (1984).

Plaksin, I.N., "Interacton of Minerals with Gases and Reagents in Flotation," Mining Engrg., March (1959).

Plaksin, I.N., Khazinskaya, G.N. and Tyurnikova, V.I., "Influence of Aeration and Oxygenation on the Flotation of Some Sulfide Minerals," Trudy Inst. Gornogo Dela, Akad Nauk S.S.S.R., 2, 206-214 (1955).

Pritzker, M.D., Yoon, R.H. and Dwight, D.W., "An ESCA Study of the Chalcopyrite Concentrate Produced by Collectorless Flotation," 54th Colloid and Surface Sci. Symp., Lehigh Univ., June (1980).

Ralston, J., Alabaster, P. and Healy, T.W., "Activation of Zinc Sulfide with Cu^{2+}, Cd^{2+}, and Pb^{2+}: III. The Mass Spectrometric Determination of Elemental Sulfur," Int. J. Min. Process., 7, 279-310 (1981).

Rao, S.R., "The Collector Mechanism in Flotation," Separ. Sci., 4, 357-391 (1969).

Ravitz, S.F., AIME Tech. Pub. No. 1147, Mining Technology, January (1940).

Ravitz, S.F. and Porter, R.R., "Oxygen-Free Flotation," AIME Tech. Pub. No. 513 (1933).

Rey, M. and Formanek, V., "Some Factors Affecting Selectivity in the Differential Flotation of Lead-Zinc Ores, Particularly in the Presence of Oxidized Lead Minerals," Int. Min. Proc. Congress, IMM, London, 343-353 (1960).

Rogers, J., "Principles of Sulfide Mineral Flotation," In: D.W. Furstenau (Editor), Froth Flotation 50th Anniversary Volume, AIME, New York, 139-167 (1962).

Sato, M., "Oxidation of Sulfide Ore Bodies, II. Oxidation Mechanisms of Sulfide Minerals at 25 C," Econ. Geol., 55, 1202-1231 (1966).

Sulman, H.L., "A Contribution to the Study of Flotation," IMM Bulletin No. 311, (1930).

Sutherland, K.L. and Wark, I.W., Principles of Flotation, Australasian Inst. Of Mining and Metall., Melbourne (1955).

Taggart, A.F., del Giuduce, G.R.M. and Ziehl, O.A., "The Case for the Chemical Theory of Flotation," Trans. AIME, 112, 348-381 (1934).

Teichmann, H., Semiconductors, Transl. by L.F. Secretan, Butterworth's, London, (1964).

Trahar, W.J., "A Laboratory Study of the Influence of Sodium Sulfide and Oxygen on the Collectorless Flotation of Chalcopyrite," Int. J. Min. Process., 11, 57ff (1983).

Vesely, C.J. and Langer, D.W., "Electronic Core Levels of the IIB-VIA Compounds," Phys. Rev. B., 4, 451-462 (1971).

Vinogradov, S.N. and Linnell, R.H., Hydrogen Bonding, Van Nostrand Reinhold, New York, (1971).

Vizsolyi, A., Veltman, H. and Forward, F.A., Trans. Met. Soc. AIME, 227, 215 (1963).

Walker, G.W., Stout III, J.V. and Richardson, P.E., "Electrochemical Flotation of Sulfides: Reactions of Chalcocite in Aqueous Solution," 56th Colloid and Surf. Sci. Symp., Virginia Tech, June 13-16 (1982).

Wark, I.W., Principles of Flotation, 1st Ed., Australasian Inst. of Mining and Metall., Melbourne (1955).

Yonezawa, T., "Experimental Study of the Adsorption and Desorption of Xanthates by Sphalerite," Trans. IMM, 70, 329-353 (1960).

Yoon, R.H., "Collectorless Flotation of Chalcopyrite and Sphalerite Ores by Using Sodium Sulfide," Int. J. Min. Process., 8, 31-48 (1981).

APPENDIX A: BATCH FLOTATION CONDITIONS AND METALLURGICAL BALANCE SHEETS

This appendix contains a summary of the conditions under which each batch flotation test was conducted, as well as the metallurgical balance sheets from these tests. The charts of the continuously monitored operating parameters, such as potential, are contained in appendix D. The procedure for determining the assays reported in the metallurgical balance sheets is given in appendix E.

Table A-1. Summary of the Conditions for Batch Flotation

Test	Pot. SHE mV	pH	[S] ppm	[O] ppm	$CuSO_4$ lb/ton	Na_2S lb/ton
1	+380	8.50	0.000	----	0.00	0.00
2	+354	8.20	0.000	8.10	0.00	0.00
3	+340	8.30	0.000	7.78	1.50	0.00
5	-058	10.50	2.800	9.50	0.00	1.50
6	+217	9.90	0.022	8.61	3.00	1.50
7	+270	5.90	0.004	8.60	1.50	1.50
8	-053	10.72	-----	8.00	0.25	1.50
9	-058	10.30	1.700	9.70	0.15	1.50
10	-023	9.94	0.980	10.50	0.00	0.50
11	+243	9.90	0.002	9.02	1.00	0.50
13	+062	7.40	0.390	7.20	0.50	0.50
14	+119	6.40	0.340	7.70	0.10	0.50
15	+003	7.60	0.920	0.90	0.25	0.50
16	+330	8.30	0.000	8.90	1.00	0.25
17	+180	8.90	0.000	8.35	0.50	0.25
18	+230	8.38	0.004	7.75	0.25	0.25
19	+090	7.60	0.099	7.00	0.10	0.25
20	+030	6.80	0.070	7.95	0.05	0.25
21	+325	8.74	0.000	7.90	0.50	0.00
22	+350	8.50	0.000	6.85	1.00	0.00
23	+310	8.50	0.000	7.10	2.00	0.00
25	+220	----	-----	8.50	0.50	0.25
26	+535	----	-----	8.80	1.50	0.25
27	+390	----	-----	8.62	2.00	0.25
28	+320	----	-----	8.85	1.50	0.50
29	+330	----	-----	8.65	2.00	0.50
30	+260	----	-----	9.00	1.00	0.50
31	+310	----	-----	9.00	1.00	0.50
32	+400	----	-----	9.20	1.00	0.50

Table A-2. Metallurgical Balance Sheets for Batch Flotation on Elmwood Sphalerite.

Test 1

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	1.28	11.03	14.12	0.89
Cl.Tail	5.15	10.80	55.62	3.49
Tailing	93.57	16.30	1525.19	95.62
Feed	100.00	15.95	1594.93	100.00

Test 2

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	0.48	15.84	7.60	0.58
Cl.Tail	7.89	13.29	104.86	7.97
Tailing	91.63	13.14	1204.02	91.45
Feed	100.00	13.16	1316.48	100.00

Test 3

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	19.54	60.00	1172.40	75.00
Cl.Tail	11.10	19.08	211.76	13.55
Tailing	69.36	2.58	178.95	11.45
Feed	100.00	15.63	1563.11	100.00

Test 5

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	0.83	6.24	5.18	0.29
Cl.Tail	10.31	12.50	128.95	7.24
Tailing	88.86	18.52	1646.05	92.47
Feed	100.00	17.80	1780.08	100.00

Table A-2 (cont.)

Test 6

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	1.28	28.91	37.00	2.24
Cl.Tail	8.65	25.70	222.28	13.49
Tailing	90.07	15.43	1389.78	84.28
Feed	100.00	16.49	1649.06	100.00

Test 7

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	1.72	17.13	29.46	1.76
Cl.Tail	10.68	14.35	153.26	9.13
Tailing	87.60	17.07	1495.33	89.11
Feed	100.00	16.78	1678.05	100.00

Test 8

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	1.02	9.84	10.04	0.59
Cl.Tail	4.64	10.57	49.04	2.89
Tailing	94.34	17.36	1637.74	96.52
Feed	100.00	16.97	1696.82	100.00

Test 9

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	0.70	8.36	5.85	0.40
Cl.Tail	6.72	11.17	75.05	5.11
Tailing	92.58	14.98	1387.07	94.49
Feed	100.00	14.68	1467.97	100.00

Test 10

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	0.61	7.79	4.75	0.33
Cl.Tail	3.58	9.98	35.73	2.49
Tailing	95.81	14.57	1396.02	97.18
Feed	100.00	14.37	1436.50	100.00

Test 11

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	18.24	54.09	986.54	69.20
Cl.Tail	10.55	8.71	91.87	6.44
Tailing	71.21	4.88	347.37	24.36
Feed	100.00	14.26	1425.78	100.00

Test 13

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	1.51	46.15	53.07	4.55
Cl.Tail	1.81	12.41	22.46	1.92
Tailing	96.68	11.29	1091.36	93.53
Feed	100.00	11.67	1166.89	100.00

Test 14

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	0.54	26.83	14.49	1.25
Cl.Tail	3.69	5.96	21.99	1.90
Tailing	95.77	11.73	1123.82	96.85
Feed	100.00	11.60	1160.30	100.00

Test 15

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	1.16	53.34	61.88	5.07
Cl.Tail	2.72	35.91	97.68	8.00
Tailing	96.12	11.04	1061.57	86.93
Feed	100.00	12.21	1221.13	100.00

Test 16

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	21.27	56.17	1194.77	84.38
Cl.Tail	3.14	2.18	6.83	0.48
Tailing	75.59	2.83	214.41	15.14
Feed	100.00	14.16	1416.02	100.00

Test 17

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	4.54	47.11	213.88	15.44
Cl.Tail	4.97	18.30	90.95	6.57
Tailing	90.49	11.94	1080.45	77.99
Feed	100.00	13.85	1385.28	100.00

Test 18

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	5.89	49.96	294.29	20.82
Cl.Tail	6.29	12.39	77.94	5.52
Tailing	87.82	11.85	1041.00	73.66
Feed	100.00	14.13	1413.23	100.00

Test 19

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	0.26	1.39	0.36	0.02
Cl.Tail	3.31	10.85	35.90	2.22
Tailing	96.43	16.37	1578.45	97.76
Feed	100.00	16.14	1614.71	100.00

Test 20

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	0.76	9.63	7.32	0.50
Cl.Tail	5.17	11.20	57.93	3.99
Tailing	94.07	14.76	1388.07	95.51
Feed	100.00	14.53	1453.32	100.00

Test 21

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	18.17	55.51	1008.62	71.23
Cl.Tail	8.86	14.22	126.00	8.90
Tailing	72.97	3.85	281.27	19.87
Feed	100.00	14.16	1415.89	100.00

Test 22

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	19.17	49.77	954.13	75.75
Cl.Tail	7.49	21.56	161.50	12.82
Tailing	73.34	1.96	143.99	11.43
Feed	100.00	12.60	1259.62	100.00

Test 23

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	19.76	56.25	1111.50	83.68
Cl.Tail	5.79	28.57	165.40	12.45
Tailing	74.45	0.69	51.31	3.87
Feed	100.00	13.28	1328.21	100.00

Test 25

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	7.24	57.78	418.32	26.54
Cl.Tail	10.07	15.29	153.96	9.77
Tailing	82.69	12.14	1003.98	63.69
Feed	100.00	15.76	1576.26	100.00

Test 26

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	20.97	61.35	1280.59	86.00
Cl.Tail	1.25	27.81	34.76	2.33
Tailing	77.88	2.23	173.67	11.67
Feed	100.00	14.89	1489.02	100.00

Test 27

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	20.15	55.65	1121.35	85.15
Cl.Tail	1.69	23.96	40.04	3.04
Tailing	78.16	1.99	155.54	11.81
Feed	100.00	13.17	1316.93	100.00

Test 28

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	20.19	56.95	1149.82	70.98
Cl.Tail	1.79	28.51	51.03	3.15
Tailing	75.02	5.37	418.97	25.87
Feed	100.00	16.20	1619.82	100.00

Test 29

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	18.67	53.70	1002.58	62.34
Cl.Tail	5.83	36.82	214.66	13.35
Tailing	75.50	5.18	391.09	24.31
Feed	100.00	16.08	1608.33	100.00

Test 30

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	16.97	57.83	981.38	67.96
Cl.Tail	10.80	7.79	84.13	5.83
Tailing	72.23	5.24	378.49	26.48
Feed	100.00	14.44	1444.00	100.00

Test 31

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	18.06	55.06	994.38	67.76
Cl.Tail	3.89	21.88	85.11	5.80
Tailing	78.05	4.97	387.92	26.44
Feed	100.00	14.67	1467.41	100.00

Test 3V

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	18.54	54.77	1015.43	68.46
Cl.Tail	13.23	24.79	327.97	22.11
Tailing	68.23	2.05	139.87	9.43
Feed	100.00	14.83	1483.27	100.00

Test R1A

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	5.74	61.91	355.36	24.32
Cl.Tail	7.11	49.53	352.16	24.10
Tailing	87.15	8.65	753.85	51.58
Feed	100.00	14.61	1461.37	100.00

Test R1B

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	7.44	63.09	469.39	27.41
Cl.Tail	4.44	45.37	201.40	11.76
Tailing	88.12	11.82	1041.55	60.83
Feed	100.00	17.12	1712.34	100.00

Test R1C

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	16.20	61.57	1078.22	72.92
Cl.Tail	18.53	12.43	230.33	16.33
Tailing	64.77	2.34	151.56	10.75
Feed	100.00	14.10	1410.11	100.00

Test R1C

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	15.86	60.24	955.41	63.25
Cl.Tail	27.06	9.65	261.13	17.29
Tailing	57.08	5.15	293.96	19.46
Feed	100.00	15.11	1510.50	100.00

Test R2A

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	8.16	50.67	413.47	25.39
Cl.Tailing	10.51	36.52	383.83	23.57
Tailing	81.33	10.22	831.19	51.04
Feed	100.00	16.28	1628.49	100.00

Test R2B

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	7.35	58.17	427.55	27.64
Cl.Tail	5.24	32.61	170.88	11.05
Tailing	87.41	10.85	948.40	61.31
Feed	100.00	15.47	1546.83	100.00

Test R2C

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	22.90	51.14	1171.11	73.63
Cl.Tail	8.25	27.30	225.23	14.16
Tailing	68.85	2.82	194.16	12.21
Feed	100.00	15.91	1590.50	100.00

Test R2D

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	17.34	52.40	906.62	62.01
Cl.Tail	27.47	8.65	237.62	16.22
Tailing	55.19	5.78	319.00	21.77
Feed	100.00	14.65	1465.24	100.00

Test P1

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	16.57	43.84	726.43	39.74
Cl.Tail	5.04	10.64	53.63	2.93
Tailing	78.39	13.37	1048.07	57.33
Feed	100.00	18.28	1828.13	100.00

Test P2

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	4.28	17.64	75.50	5.16
Tailing	95.72	14.50	1387.94	94.84
Feed	100.00	14.63	1463.44	100.00

Test P3

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	10.50	44.22	464.32	30.27
Tailing	89.49	11.95	1069.41	69.73
Feed	100.00	15.34	1533.73	100.00

Test P4

Product	Weight %	% Zinc	Unit Zn	Distribution
Conc.	2.78	11.11	30.89	2.22
Tailing	97.22	14.01	1362.05	97.78
Feed	100.00	13.93	1392.94	100.00

APPENDIX B: MICROFLOTATION CONDITIONS

Test	pH	Pot. (SHE)	Recovery	$CuSO_4$
31	5.70	+432	35.40	0
32	11.25	-173	6.90	0
33	10.20	-028	5.70	0
34	9.60	+047	7.80	0
35	6.87	+272	22.70	0
36	6.90	+644	16.30	0
38	6.50	+615	12.10	0
39	5.46	+590	81.42	5×10^{-5}
40	7.62	+266	90.99	"
41	9.55	+102	64.75	"
42	10.32	-006	33.33	"
43	11.62	-332	7.63	"
44	7.30	+732	0.00	"
46	5.60	+502	85.35	"
47	6.70	+412	91.24	"
48	5.42	+400	94.44	5×10^{-3}
49	10.94	-248	44.04	"
50	11.24	-383	2.50	"
51	9.81	-076	83.33	"
52	8.96	+150	97.12	"

Test	pH	Pot. (SHE)	Recovery	$CuSO_4$
53	6.07	+794	1.55	5×10^{-3}
54	9.67	+489	74.19	"
55	10.97	-177	76.85	"
56	5.53	+374	95.54	5×10^{-2}
57	10.91	-212	21.10	"
58	11.68	-437	1.94	"
59	10.07	-103	56.76	"
60	10.10	-044	80.51	"
61	10.03	+118	43.22	"
62	8.76	+198	51.72	"
63	9.04	+272	29.82	"
64	5.99	+747	54.31	"
65	6.14	+445	60.00	"
66	8.90	+301	36.36	"
67	9.03	+055	88.89	"
68	6.08	+534	67.18	"
69	4.66	+395	48.72	"
94	4.00	+356	63.39	0
95	4.00	-002	18.10	0
96	4.00	+227	66.36	0

Test	pH	Pot. (SHE)	Recovery	$CuSO_4$
97	4.00	-437	12.26	0
98	4.00	-047	14.16	0
99	4.00	+1015	23.58	0
100	4.00	+617	51.40	0
101	4.00	+748	49.49	0
103	4.00	+410	98.94	5×10^{-5}
104	4.00	+054	88.68	"
105	4.00	+153	96.15	"
106	4.00	+227	95.15	"
107	4.00	+343	92.66	"
108	4.00	+439	95.33	"
109	4.00	+864	95.50	"
110	4.00	+740	95.37	"
111	4.00	+468	95.28	0
112	4.00	+033	95.41	0
113	4.00	-034	43.64	0
114	4.00	+038	93.04	5×10^{-5}
115	7.55	-075	83.64	0
116	4.60	+068	86.99	0
117	4.00	+532	96.12	5×10^{-5}
118	4.00	-040	86.27	5×10^{-5}

Test	pH	Pot. (SHE)	Recovery	$CuSO_4$
119	7.00	+397	96.40	0
120	7.00	-170	73.79	0
121	7.00	-270	23.21	0
122	7.00	-073	93.52	0
123	7.00	+013	94.55	0
124	7.00	+166	95.50	0
125	7.00	+577	96.23	0
126	7.00	+703	43.81	0
127	7.00	+342	96.12	0
128	7.00	+450	95.73	0
129	7.00	+491	94.64	5×10^{-5}
130	7.00	-273	32.73	"
131	7.00	-151	94.39	"
132	7.00	-070	93.52	"
133	7.00	+098	97.03	"
134	7.00	+687	91.26	"
135	7.00	+387	95.10	"
136	7.00	+569	95.24	"
137	7.00	+277	96.00	"
138	10.00	+341	6.19	0
139	10.00	-425	7.41	0
140	10.00	-066	2.86	0
141	10.00	+149	3.00	0
142	10.00	+580	0.00	0
143	10.00	+649	0.00	0
144	10.00	+680	0.00	0
145	10.00	+347	93.01	5×10^{-5}
146	10.00	-353	7.14	"
147	10.00	-121	39.58	"

Test	pH	Pot. (SHE)	Recovery	$CuSO_4$
148	10.00	+355	91.67	5×10^{-5}
149	10.00	-100	51.55	"
150	10.00	-066	21.65	"
151	10.00	-030	38.14	"
152	10.00	+104	65.66	"
153	10.00	+235	67.01	"
154	10.00	+645	1.03	"
155	10.00	+478	73.96	"
156	10.00	+578	56.44	"
157	10.00	+329	98.97	5×10^{-3}
158	10.00	-115	30.30	"
159	10.00	-046	44.44	"
160	10.00	+265	10.20	"
161	10.00	+071	61.05	"
162	10.00	+640	0.00	"
163	10.00	+569	22.22	"
164	10.00	+510	82.47	"
165	10.00	+445	67.31	"
166	10.00	+222	51.35	"

Test	pH	Pot. (SHE)	Recovery	$CuSO_4$
167	7.00	+551	14.43	0
168	7.00	-111	10.42	0
169	7.00	-251	5.21	0
170	7.00	+025	13.54	0
171	7.00	+252	10.42	0
172	7.00	+142	14.29	0
173	7.00	+803	0.99	0
174	7.00	+324	19.39	0
175	7.00	+452	21.34	0
176	7.00	+554	97.94	5×10^{-5}
177	7.00	-227	23.30	"
178	7.00	-069	75.00	"
179	7.00	+346	76.53	"
180	7.00	+007	91.18	"
181	7.00	+202	94.90	"
182	7.00	+252	97.98	"
183	7.00	+472	98.10	"
184	7.00	+800	2.65	"
185	7.00	+703	96.40	"
186	10.00	+312	91.75	"

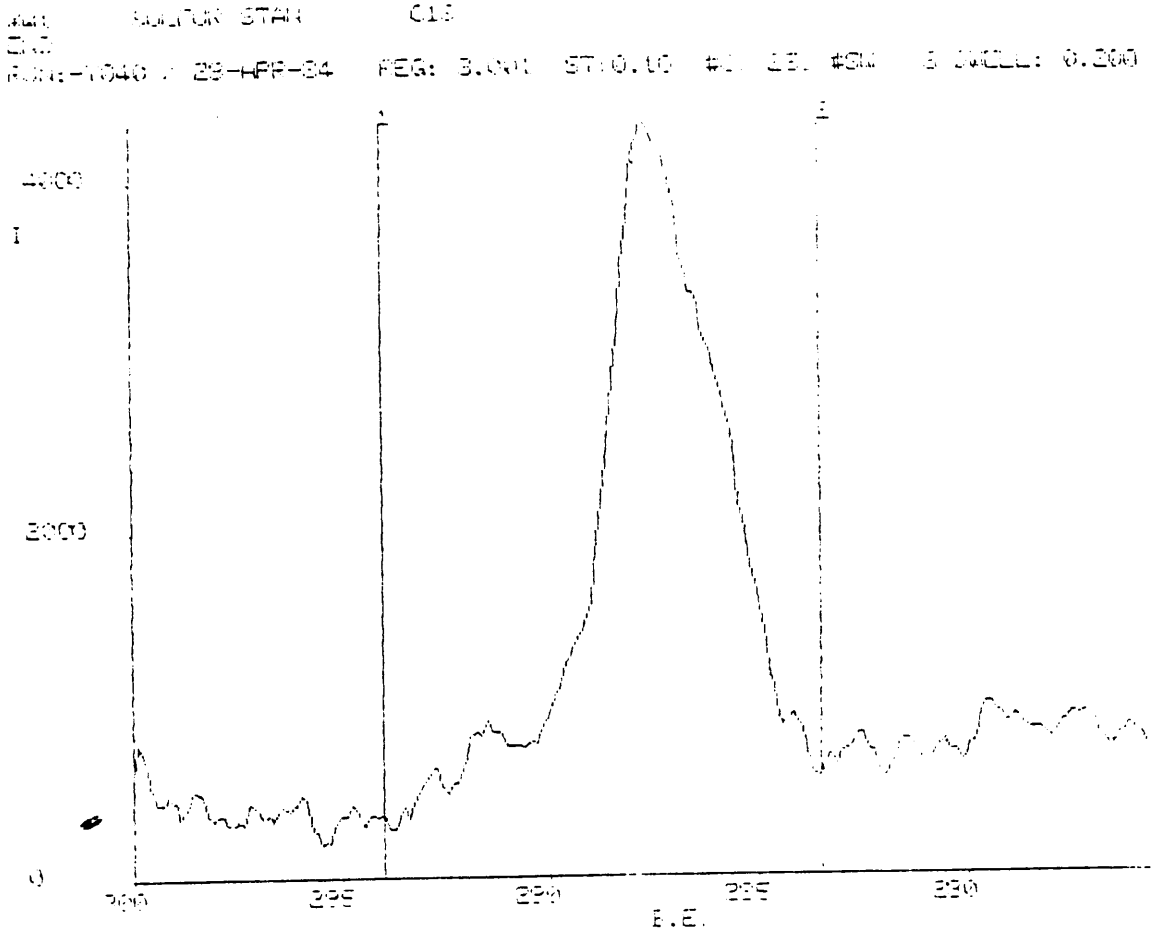
Test	pH	Pot. (SHE)	Recovery	$CuSO_4$
187	10.00	+194	73.74	$5x10^{-5}$
188	10.00	+140	84.21	$5x10^{-3}$
189	10.00	+257	91.67	"
190	10.00	+307	87.50	"
191	10.00	-257	16.35	"

APPENDIX C: XPS SPECTRA AND CALCULATIONS

Since most specimens exhibited complex carbon-1s peaks, the assignment of peak location for calculation of sample charging was not trivial. The assignment of particular peak locations was based on an analysis of the geometry of the carbon-1s peaks, an assumption that sample charging would be relatively consistent between samples, and a practical examination of the identity of the various sulfur species indicated using different charge corection factors. Peak location and the differnece in binding energy between peaks in the Sulfur-2p region as given in the literature were used to correlate the data obtained in the present work and to define the charge correction factor for each sample. The assignments of the binding energy for the carbon-1s peak thus calculated result in reasonable identities for the sulfur species found on each sample.

Table C-1. The binding energy of the carbon-1s peak and the charge correction factor (arrived by assigning the standard carbon peak to 284.9 eV) for the samples of Elmwood sphalerite and a sulfur standard.

Sample	Carbon-1s Peak	Charge Correction
Sulfur std.	287.7 eV	2.8 eV
1C	291.9	7.0
2T	291.1	6.2
3T	292.0	7.1
4T	290.8	5.9
5C	291.3	6.4
6T	290.0	5.1


C1S
29-APR-84
4000
3000
0
295
290
285
280
B.E.

RUN : Y040 / 29-APR-84
SAMPLE: 1
NAME : SULFUR STND
TITLE : DR YOON
13KV 20MA SLIT=2 CUR=9.0

EXCITATION : MG ANALYSER MODE: FRR
SCAN MODE : T FACTOR : 0

MAGNIFICATION: L RESOLUTION: M

BASELINE THRESHOLD: 0 MIN. PEAK WIDTH: 1.00

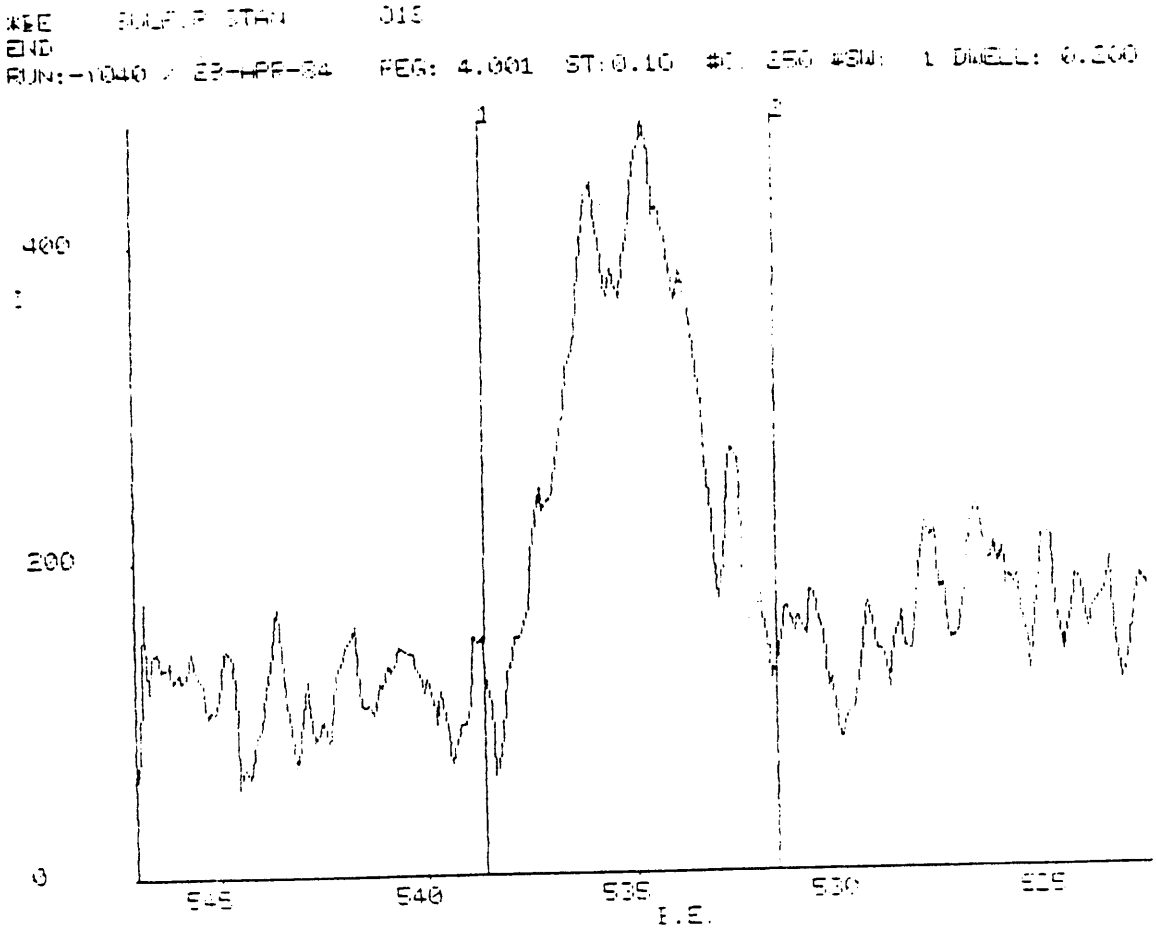
REGION: 3 - WITH MARKERS

ELMT	K.E.	STEP	DWELL	#CHAN	#AVG
XC1	968.60	0.10	0.200	250	3

SCAN: 1

START E.V. : 953.60 END E.V. : 978.50

PEAK	K.E.	B.E.	MAX	AREA	FWHH
1	965.90	287.70	3890	134816	3.00


END
RUN:-1040 / 23-HPF-84 PEG: 4.001 ST:0.10
1
2
400
200
0
545
540
535
530
525
I.E.

RUN : 1040 / 23-APR-84
SAMPLE: 1
NAME : SULFUR STND
TITLE : DR YOON
13KV 20MA SLIT=2 CUR=9.0

EXCITATION : MG ANALYSER MODE: FRR
SCAN MODE : T FACTOR : 0

MAGNIFICATION: L RESOLUTION: M

BASELINE THRESHOLD: 0 MIN. PEAK WIDTH: 1.00

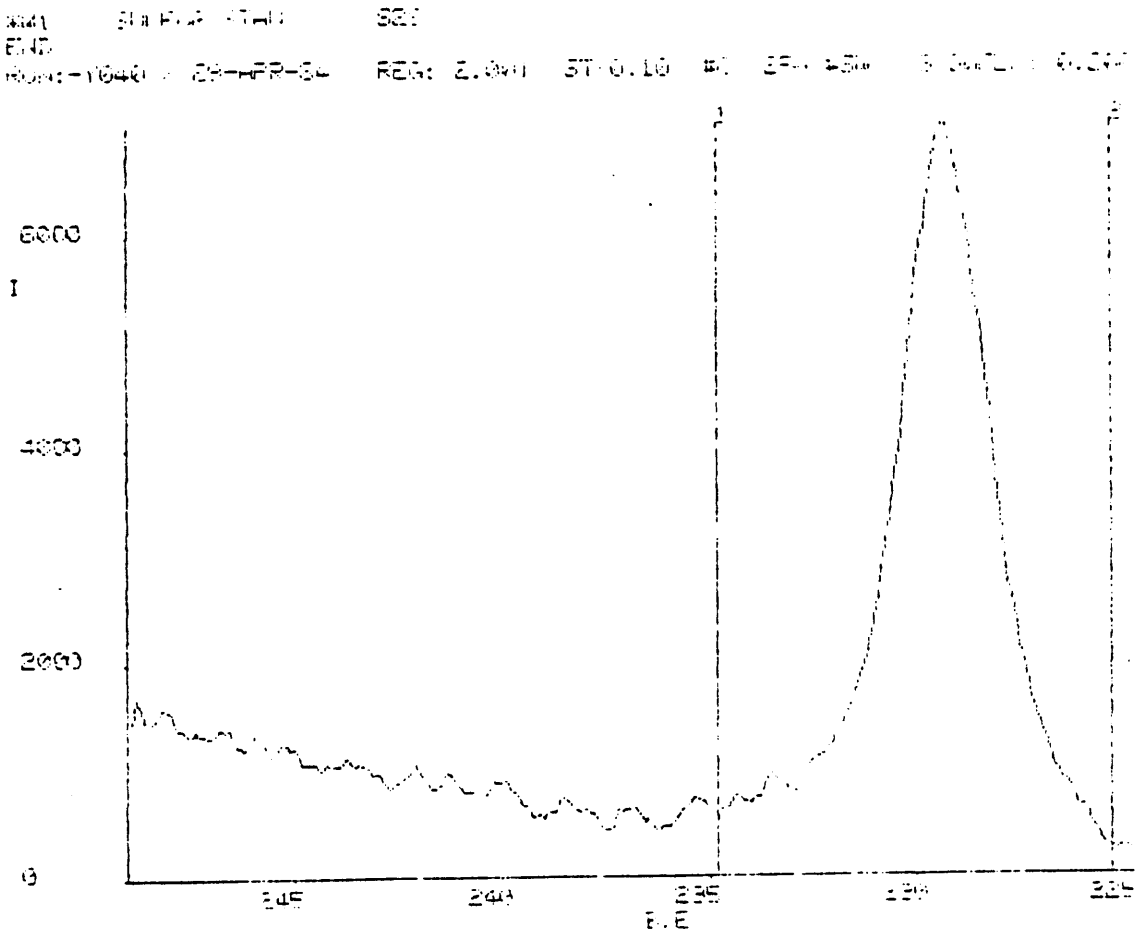
REGION: 4 - WITH MARKERS

ELMT	K.E.	STEP	DWELL	#CHAN	#AVG
X01	721.60	0.10	0.200	250	1

SCAN: 1

START E.V. : 706.60 END E.V. : 731.50

PEAK	K.E.	B.E.	MAX	AREA	FWHH
1	718.80	534.80	357	12417	3.40


6000
I
4000
2000
0
245
240
235
230
225
E.E

RUN : [illegible]
SAMPLE:
NAME : [illegible]
TITLE : [illegible]
15kV 20mA SLIT=2 CUR=3.0

EXCITATION : MG ANALYSER MODE: FRR
SCAN MODE : T FACTOR : 0

MAGNIFICATION: [illegible] RESOLUTION: M

BASELINE THRESHOLD: 0 MIN PEAK WIDTH: 1.00

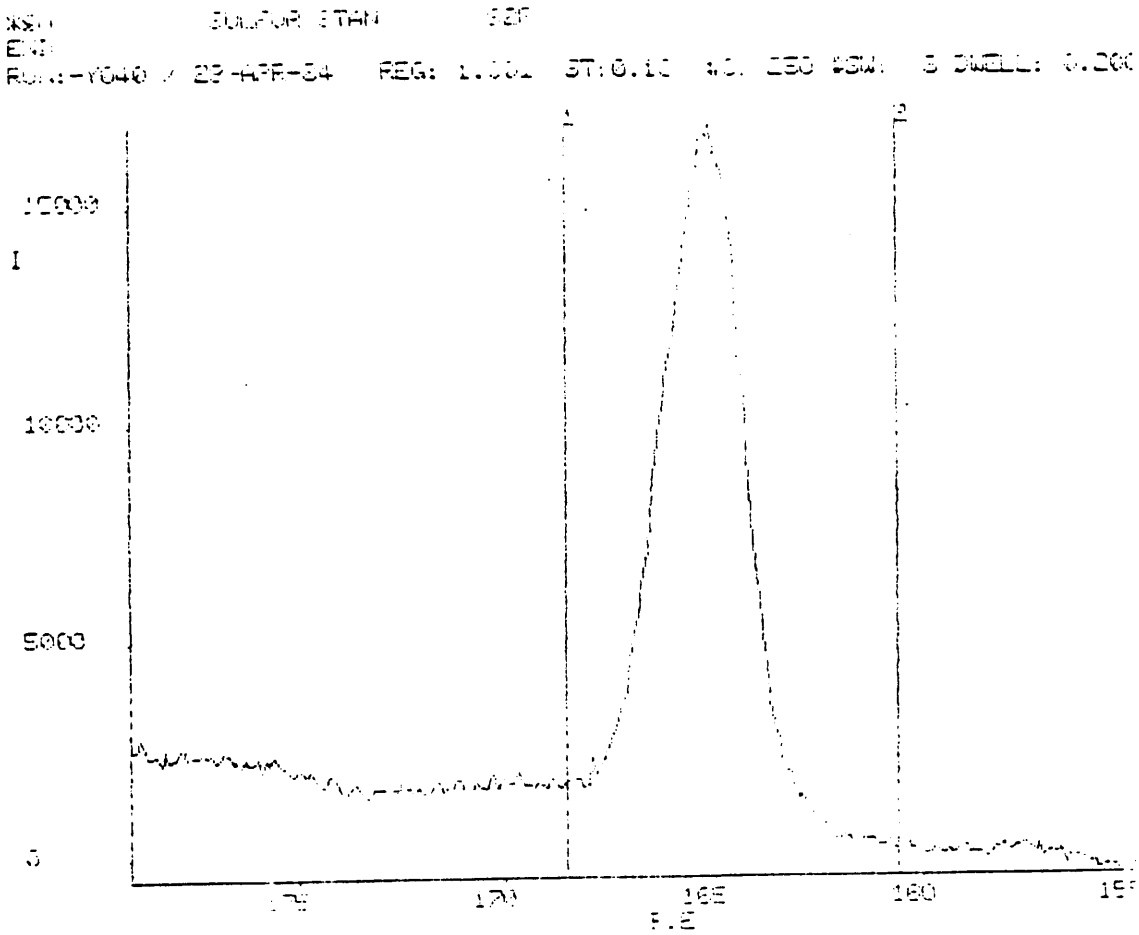
REGION: 2 - WITH MAPPER

ELMT	K.E.	STEP	DWELL	#CHAN	#AVG
XS2S	1019.60	0.10	0.200	250	3

SCAN: 1

START E.V. : 1004.60 END E.V. : 1029.50

PEAK	K.E.	B.E.	MAX	AREA	FWHH
1	1024.30	225.30	6522	150734	2.40


10000
I
10000
5000
0
170
180
160
F.E

RUN : Y[illegible] / 23-APR-84
SAMPLE: 1
NAME : SULFUR STND
TITLE : DR YOUN
13.0 20MA [illegible]T=2 [illegible]=3.0

EXCITATION : MG ANALYSER MODE: FRP
SCAN MODE : T FACTOR : 0

MAGNIFICATION: L RESOLUTION: M

BASELINE THRESHOLD: 0 MIN. PEAK WIDTH: 1.00

REGION: 1 - WITH MARKERS

ELMT	K.E.	STEP	DWELL	#CHAN.	#AVG
XS	1088.60	0.10	0.200	250	3

SCAN: 1

START E.V. : 1074.60 END E.V. : 1099.50

PEAK	K.E.	B.E.	MAX	AREA	FWHH
1	1088.50	165.10	15756	373120	2.20

RUN	REG	SCAN	STEP	#CH
Y040	1	1	.10	32

ELMT	K.E.	DWELL
NB	1089.00	.200

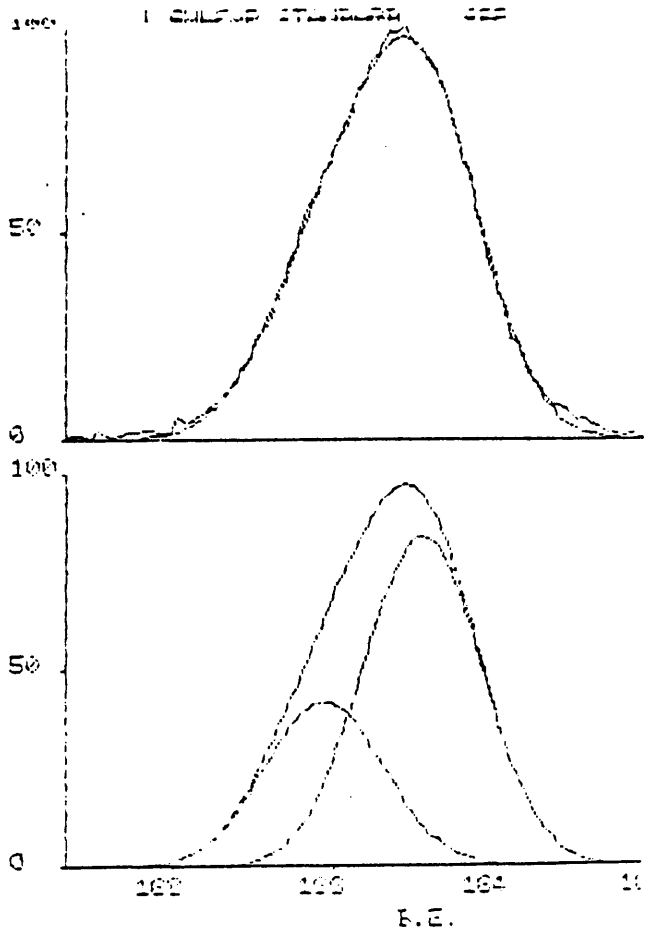
START EV: 182.30
END EV: 181.20

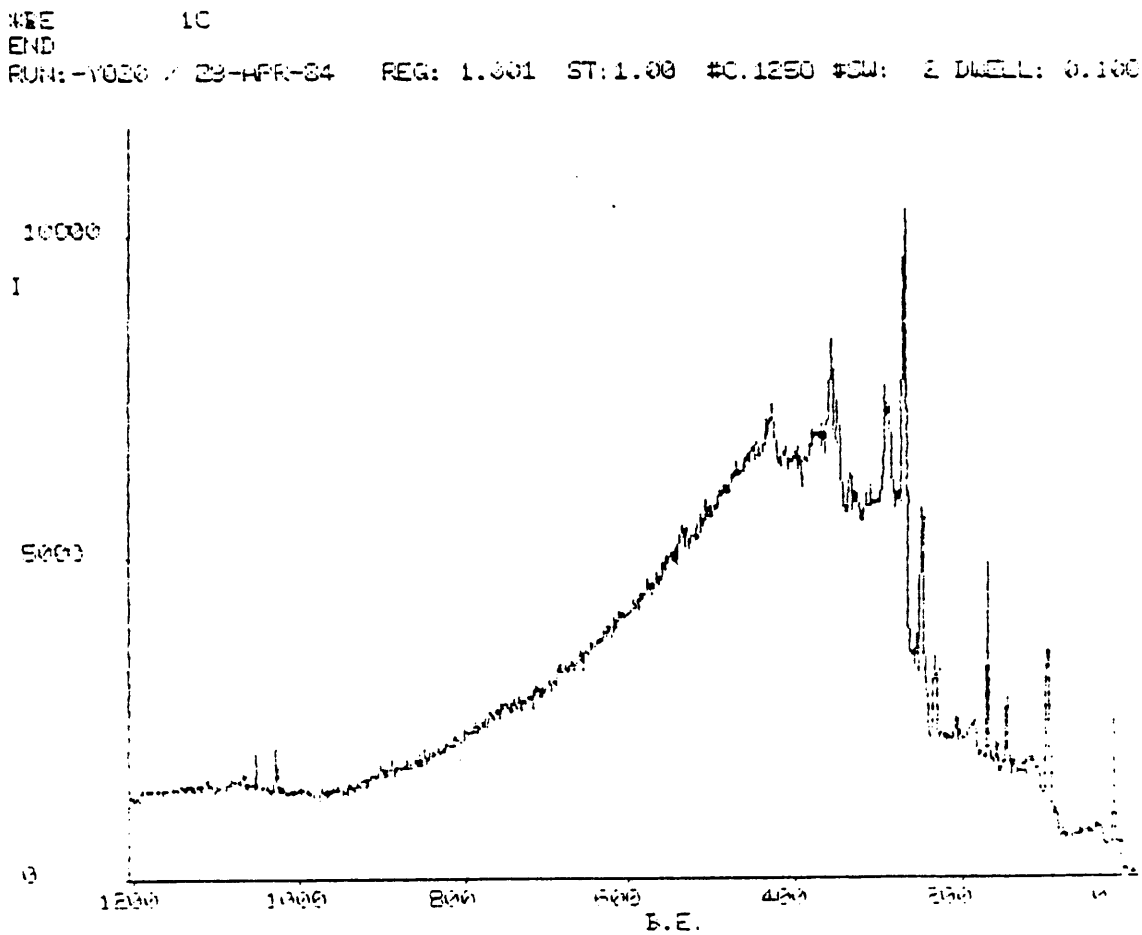
100% AREA =270832

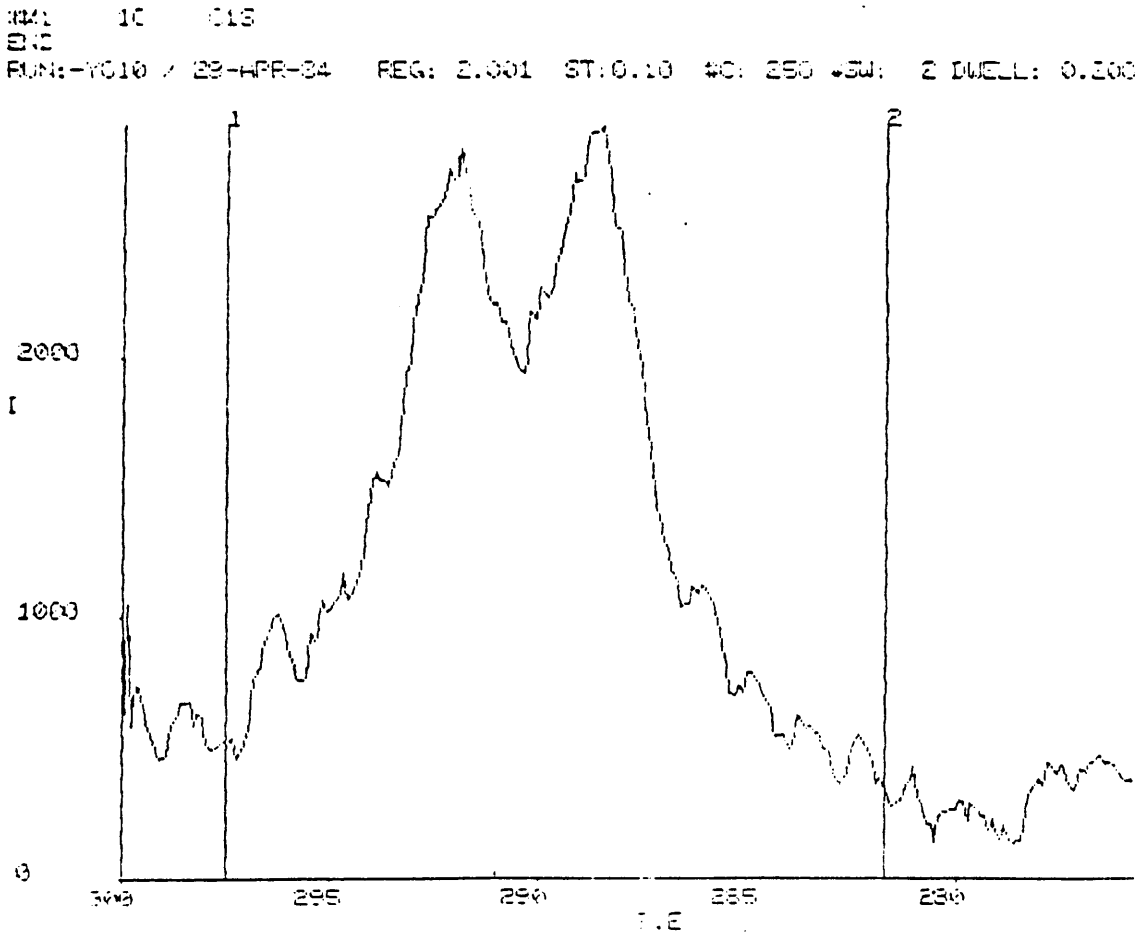
100% INTENSITY =15200

FIT=4

PK	ENERGY	MAX	FWHM	AREA
1G	186.10	42.00	1.70	32.7
2G	184.90	84.00	1.70	65.4




END
RUN:-Y036 / 29-APR-84 REG: 1.001 ST:1.00 #C.1250 #CW: 2 DWELL: 0.100
10000
I
5000
0
12000
10000
8000
6000
4000
2000
0
B.E.


RUN:-Y010 / 29-APR-84 REG: 2.001 ST:0.10 #C: 250 #SW: 2 DWELL: 0.200
1
2
2000
1000
0
295
290
285
280

RUN : Y010 / 29-APR-84
SAMPLE: 1
NAME : 1C
TITLE : DR YOON
13KV 20MA SLIT=2 CUR=9.0

EXCITATION : MG ANALYSER MODE: FRR
SCAN MODE : T FACTOR : 0

MAGNIFICATION: L RESOLUTION: M

BASELINE THRESHOLD: 0 MIN. PEAK WIDTH: 1.00

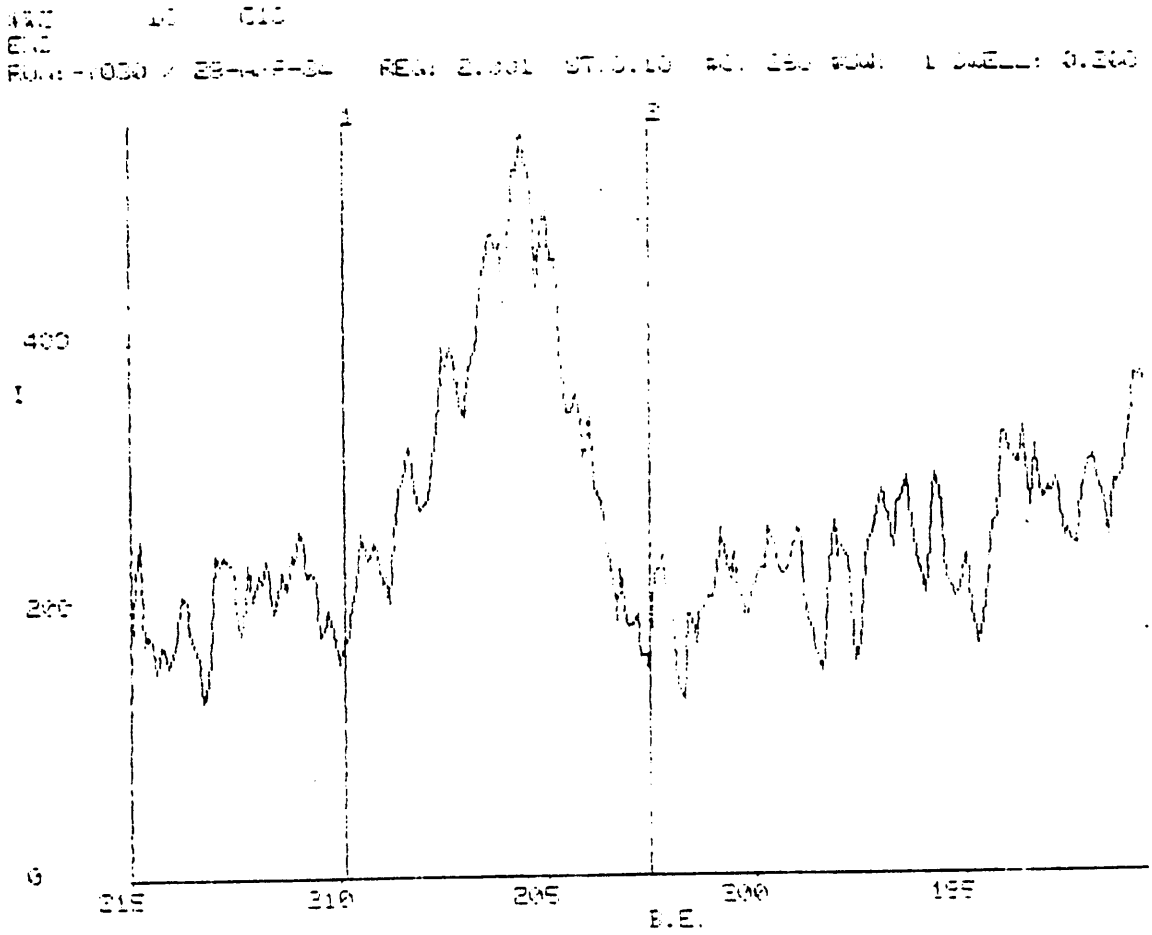
REGION: 2 - WITH MARKERS

ELMT	K.E.	STEP	DWELL	#CHAN	#AVG
XC1	968.60	0.10	0.200	250	2

SCAN: 1

START E.V. : 953.60 END E.V. : 978.50

PEAK	K.E.	B.E.	MAX	AREA	FWHH
1	965.00	288.60	2507	164405	6.00


400
200
0
215
210
205
200
195
B.E.

RUN : Y030 / 23-APR-84
SAMPLE: 1
NAME : 1C
TITLE : DR YOON
13KV 20MA SLIT=2 CUR=0.0

EXCITATION : MG ANALYSER MODE: FRR
SCAN MODE : T FACTOR : 0

MAGNIFICATION: L RESOLUTION: M

BASELINE THRESHOLD: 0 MIN. PEAK WIDTH: 1.00

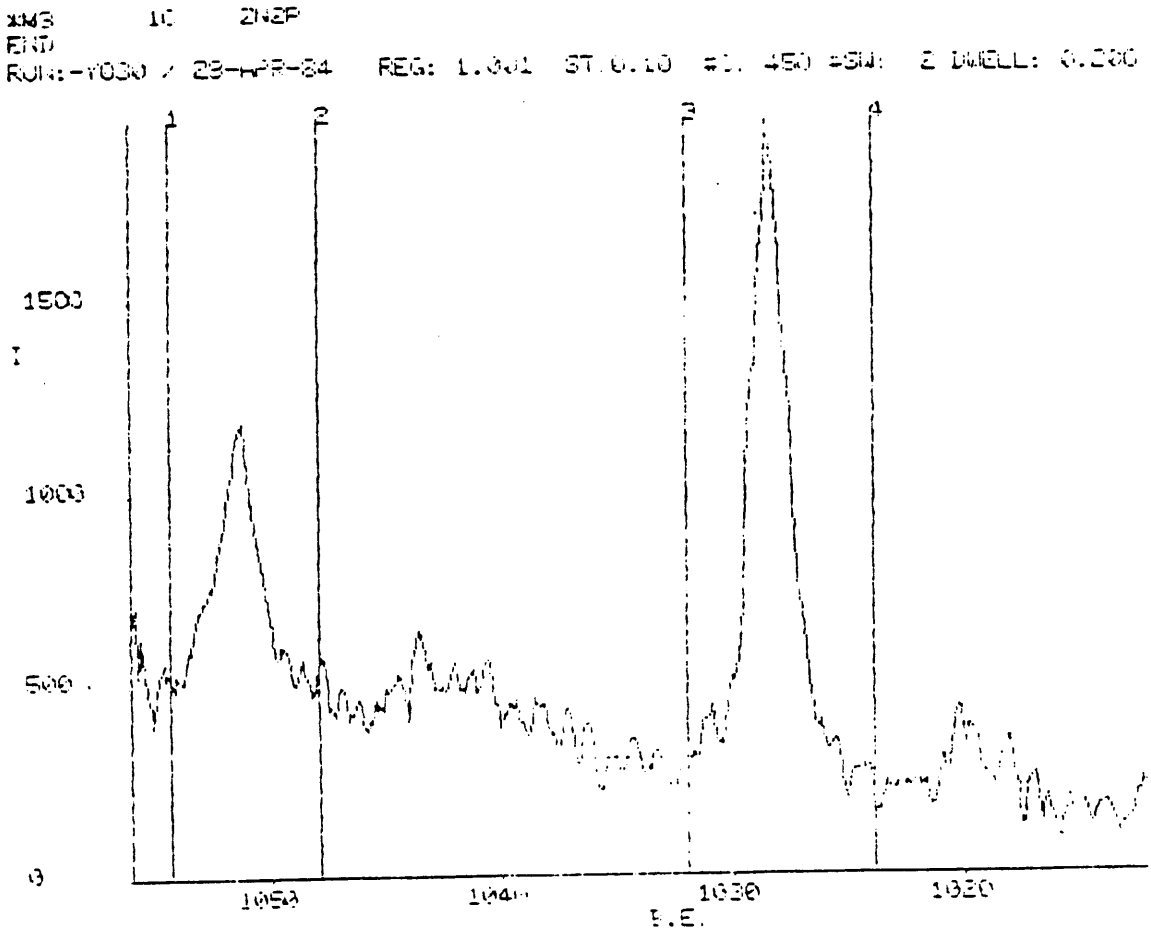
REGION: 2 - WITH MARKERS

ELMT	K.E.	STEP	DWELL	#CHAN	#AVG
XCL	1053.60	0.10	0.200	250	1

SCAN: 1

START E.V. : 1038.60 END E.V. : 1063.50

PEAK	K.E.	B.E.	MAX	AREA	FWHH
1	1048.00	205.60	376	12202	3.10


XMB 10 2N2P
END
RUN:-Y030 / 23-APR-84 REG: 1.001 ST.0.10 #1. 450 #SW: 2 DWELL: 0.200
1
2
3
4
1500
I
1000
500
0
1050
1040
1030
1020
B.E.

RUN : Y030 / 28-APR-84
SAMPLE: 1
NAME : 1C
TITLE : IR YOON
15KV 20mA SLIT=2 CUR=3.0

EXCITATION : MG ANALYSER MODE: FRR
SCAN MODE : T FACTOR : 0

MAGNIFICATION: L RESOLUTION: M

BASELINE THRESHOLD: 0 MIN. PEAK WIDTH: 1.00

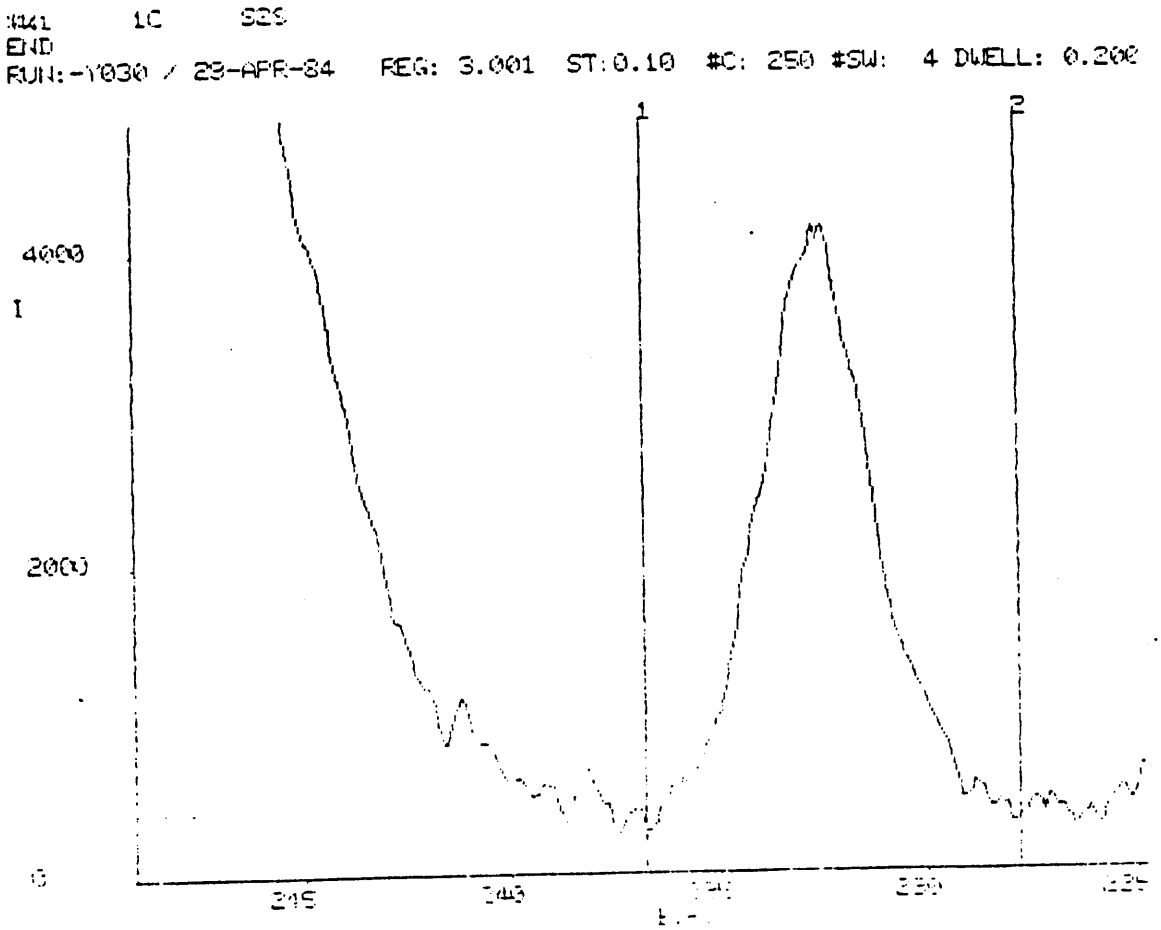
REGION: 1 - WITH MARKERS

ELMT	K.E.	STEP	DWELL	#CHAN	#AVG
XZN	232.60	0.10	0.200	450	2

SCAN: 1

START E.V. : 197.80 END E.V. : 242.50

PEAK	K.E.	B.E.	MAX	AREA	FWHM
1	202.30	1051.30	881	14524	1.30
2	225.30	1028.30	1721	33146	1.90


:441 1C 325
END
RUN:-Y030 / 23-APR-84 REG: 3.001 ST:0.10 #C: 250 #SW: 4 DWELL: 0.200
1
2
4000
I
2000
0
315
340
330

[illegible] : [illegible]
[illegible] :
[illegible] : 10
[illegible] : [illegible]
15KV [illegible] SLIT=2 CUR=9.0

EXCITATION : MA ANALYSER MODE: FRR
SCAN MODE : T FACTOR : 0

[illegible] RESOLUTION: M

BASELINE THRESHOLD: 0 Min. PEAK WIDTH: 1.00

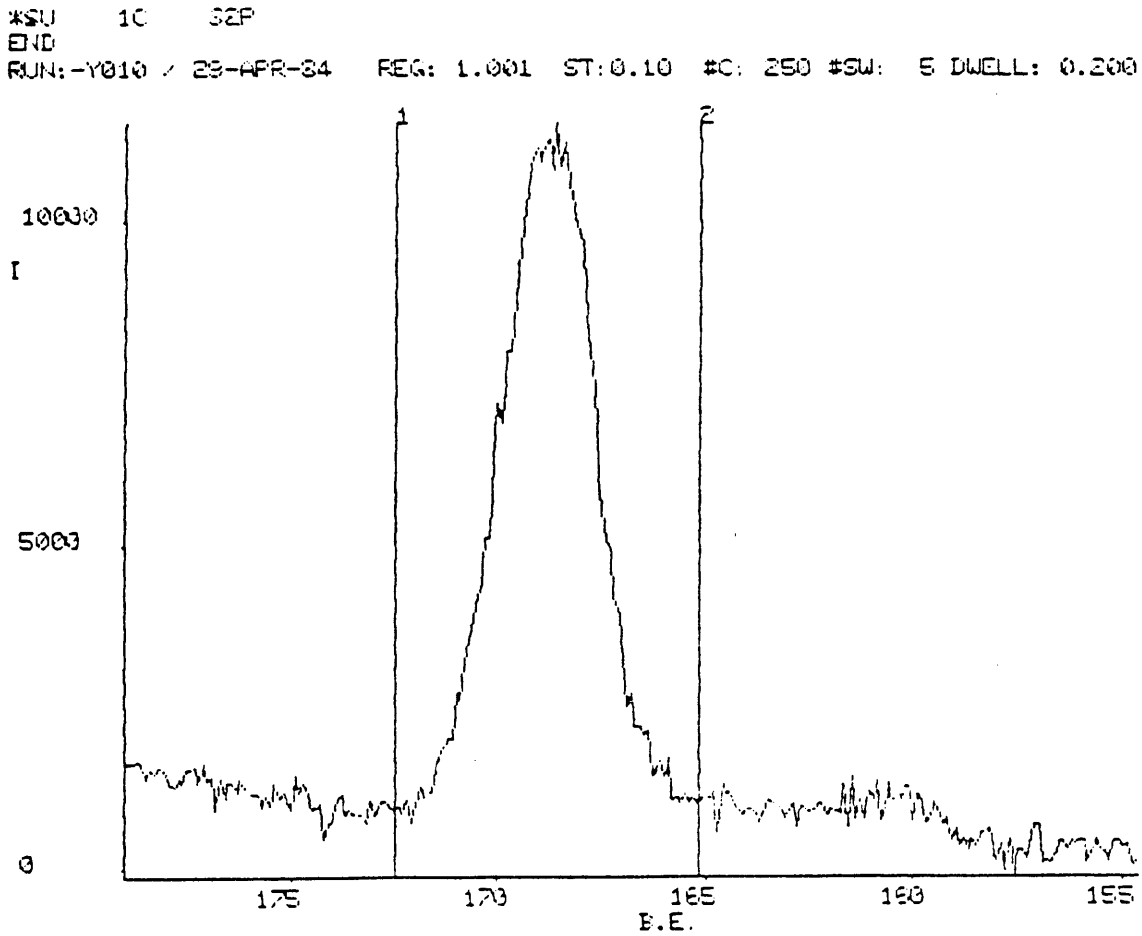
REGION: 3 - WITH MARKERS

ELMT	K.E.	STEP	DWELL	#CHAN	#AVG
XS25	1019.60	0.10	0.200	350	4

SCAN: 1

START E.V. : 1004.60 END E.V. : 1023.50

PEAK	K.E.	B.E.	MAX	AREA	FWHM
1	1021.00	330 E.V.	3006	125196	2.94


*SU 1C 32P
END
RUN:-Y010 / 23-APR-84 REG: 1.001 ST:0.10 #C: 250 #SW: 5 DWELL: 0.200
1
2
10000
I
5000
0
175
170
165
160
155
B.E.

RUN : Y010 / 23-APR-84
SAMPLE: 1
NAME : 1C
TITLE : DR YOON
13KV 20MA SLIT=2 CUR=9.0

EXCITATION : MG ANALYSER MODE: FRR
SCAN MODE : T FACTOR : 0

MAGNIFICATION: L RESOLUTION: M

BASELINE THRESHOLD: 0 MIN. PEAK WIDTH: 1.00

REGION: 1 - WITH MARKERS

ELMT	K.E.	STEP	DWELL	#CHAN	#AVG
XS	1028.60	0.10	0.200	250	5

SCAN: 1

START E.V. : 1074.60 END E.V. : 1099.50

PEAK	K.E.	B.E.	MAX	AREA	FWHH
1	1085.00	168.60	10302	284414	2.60

RUN	REG	SCAN	STEP	#CH
Y010	1	1	.10	88

ELMT	K.E.	DWELL
XS	1089.80	.200

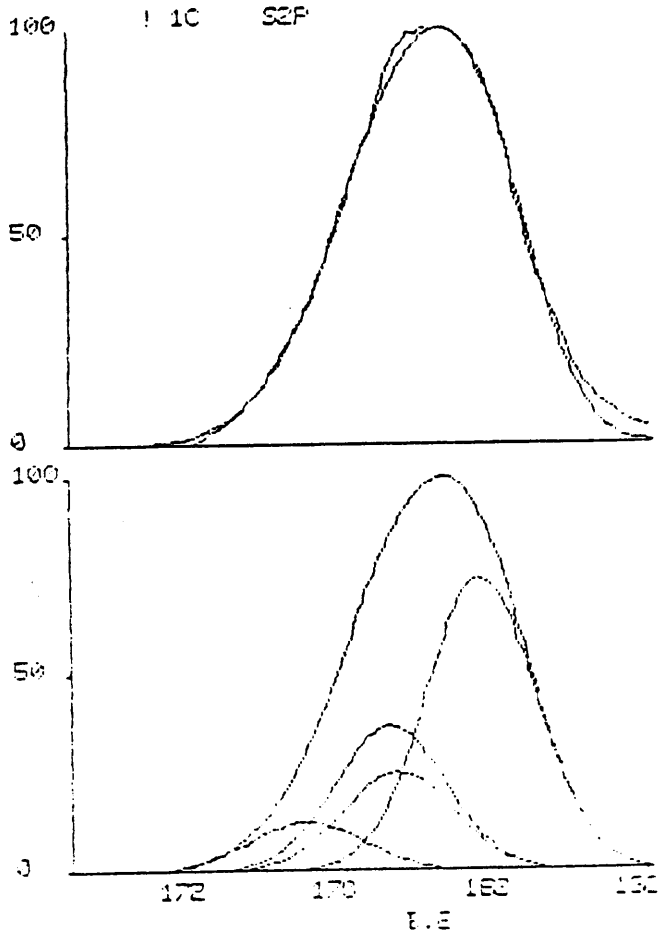
START EV: 173.80
END EV: 164.90

100% AREA =202932

100% INTENSITY =10200

FIT=10

PK	ENERGY	MAX	FWHM	AREA
1G	170.50	12.30	1.70	8.1
2G	168.30	25.00	1.70	16.3
3G	165.40	37.00	1.70	24.2
4G	162.20	74.00	1.70	48.4



RUN	REG	SCAN	STEP	#CH
X010	1	1	.10	60

ELMT	K.E.	DWELL
XE	1000.00	.200

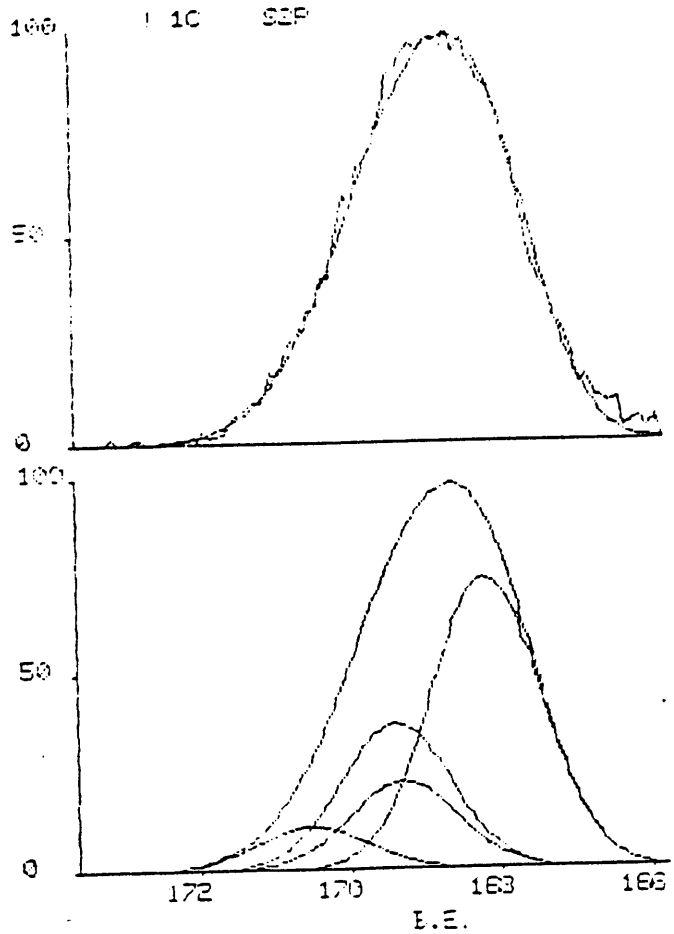
START EV: 173.60
END EV: 164.90

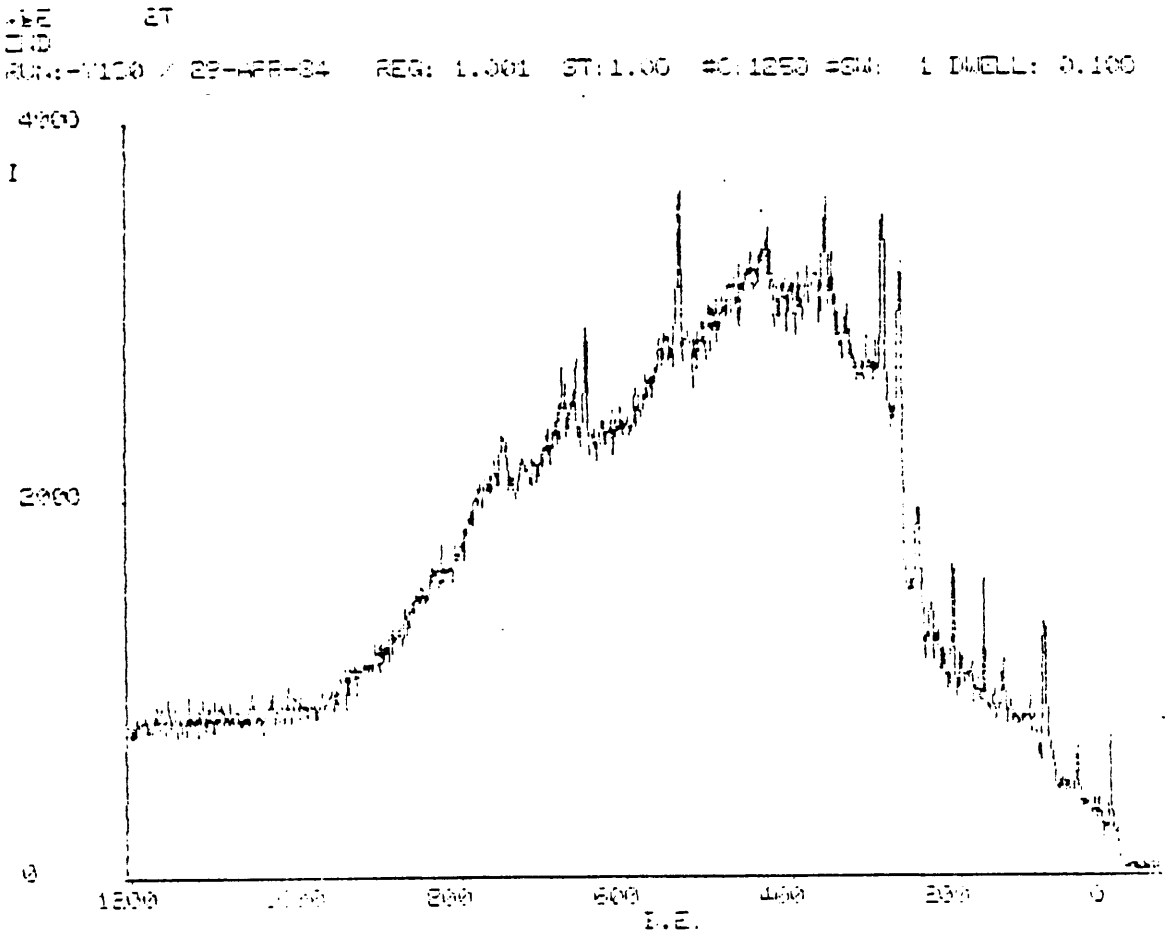
100% AREA =231604

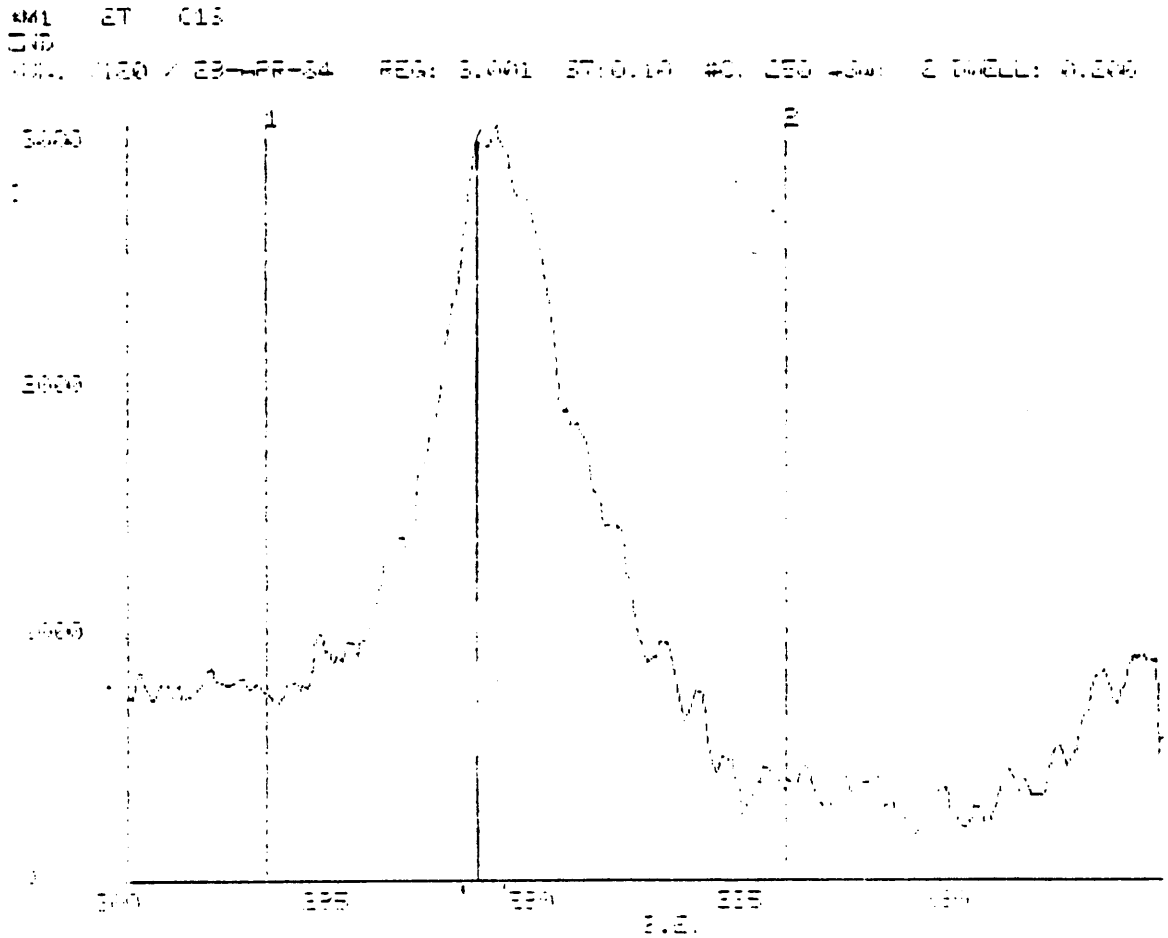
100% INTENSITY =10510

FIT=18

PK	ENERGY	MAX	FWHH	AREA
1G	170.50	11.00	1.70	7.4
2G	169.30	22.00	1.70	14.5
3G	169.40	37.00	1.70	25.0
4G	168.20	74.00	1.70	50.1




RUN:-7130 / 29-APR-84 REG: 1.001 ST:1.00 #C:1250 #SW: 1 DWELL: 0.100
4000
I
2000
0
1000
2000
3000
4000
5000
6000
7000
I.E.


1
2

RUN : Y120 / 28-APR-84
SAMPLE: 1
NAME : 27
TITLE : DR YOON
13KV 20MA SLIT=2 CUR=3.0

EXCITATION : MG ANALYSER MODE: FRR
SCAN MODE : T FACTOR : 0

MAGNIFICATION: L RESOLUTION: M

BASELINE THRESHOLD: 0 MIN. PEAK WIDTH: 1.00

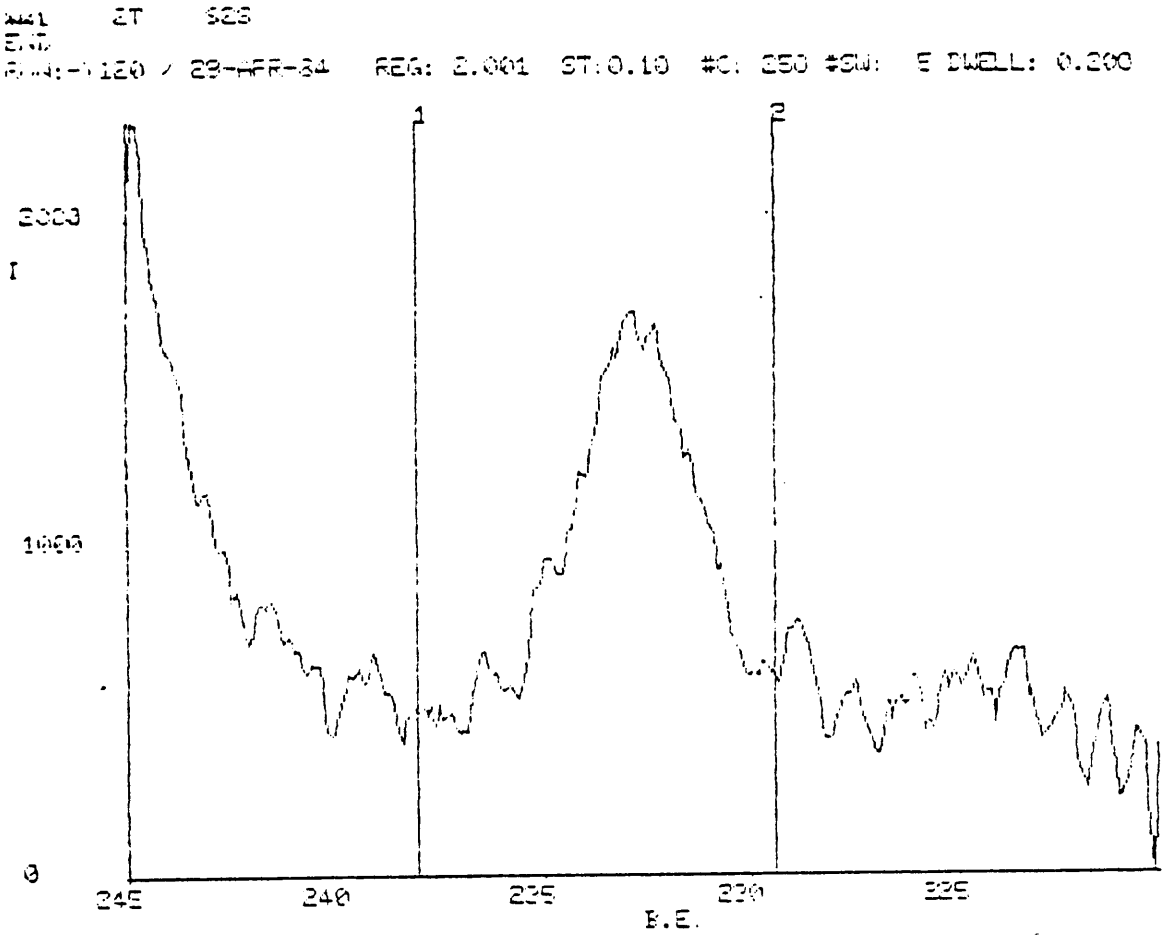
REGION: 3 - WITH MARKERS

SLIT	K.E.	STEP	DWELL	#CHAN	#AVG
XC1	933.80	0.10	0.200	250	2

SCAN: 1

START E.V. : 953.80 END E.V. : 978.50

PEAK	K.E.	B.E.	MAX	AREA	FWHH
1	962.50	291.10	2513	111878	3.50


ZT
RAN:-1120 / 29-APR-84
REG: 2.001
ST:0.10
#C: 250
#SW:
E DWELL: 0.200
1
2
2000
I
1000
0
245
240
235
230
225
B.E.

RUN : Y120 / 29-APR-84
SAMPLE: 1
NAME : 2T
TITLE : DR YOON
13KV 20MA SLIT=2 CUR=3.0

EXCITATION : MG ANALYSER MODE: FRR
SCAN MODE : T FACTOR : 0

MAGNIFICATION: L RESOLUTION: M

BASELINE THRESHOLD: 0 MIN. PEAK WIDTH: 1.00

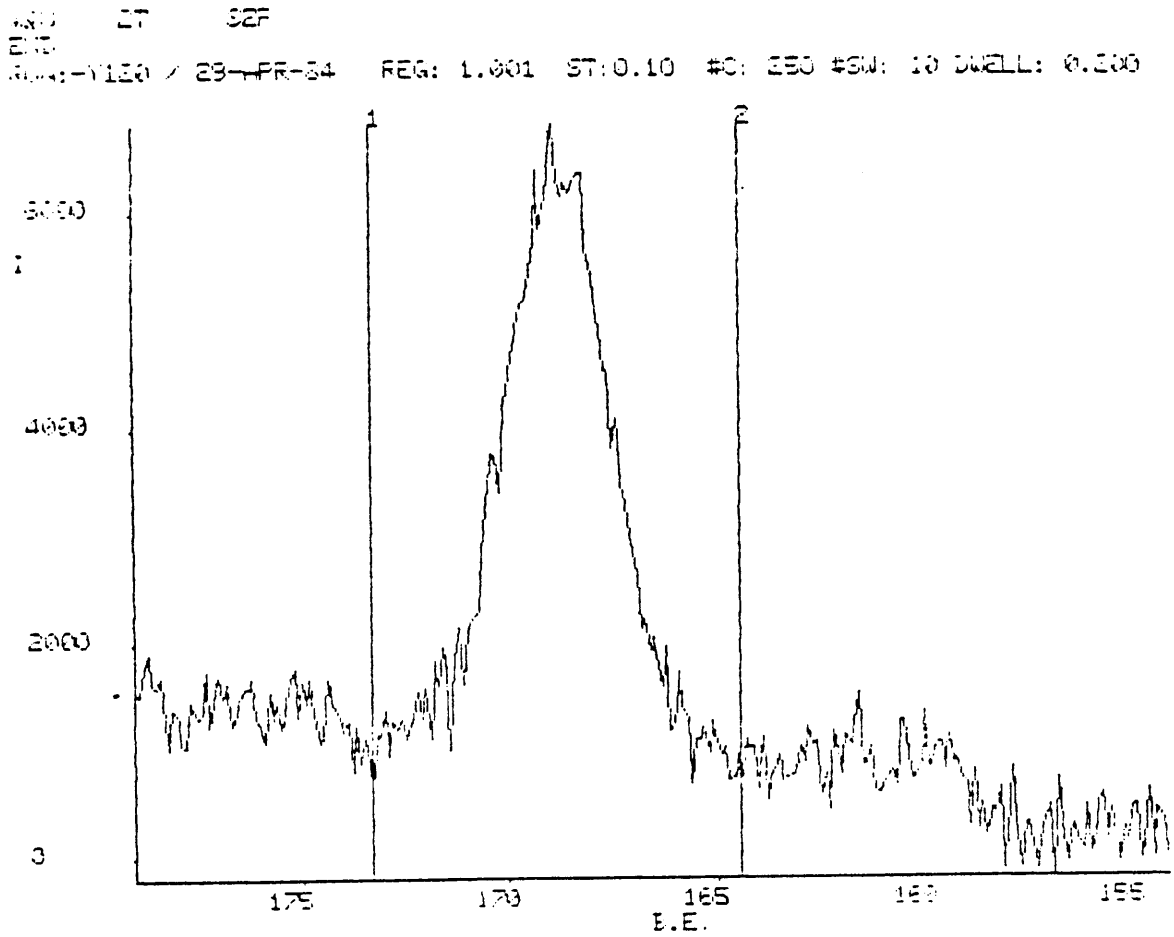
REGION: 2 - WITH MARKERS

ELMT	K.E.	STEP	DWELL	#CHAN	#AVG
XE2I	1023.60	0.10	0.200	250	5

SCAN: 1

START E.V. : 1002.60 END E.V. : 1033.50

PEAK	K.E.	B.E.	MAX	AREA	FWHH
1	1020.70	232.80	1178	30379	3.10


2T
S2F
FEG: 1.001 ST:0.10 #C: 250 #SW: 10 DWELL: 0.200
1
2
6000
4000
2000
0
175
170
165
160
155
B.E.

RUN : Y120 / 29-APR-84
SAMPLE: 1
NAME : 2T
TITLE : DR YOON
13KV 20MA SLIT=2 CUR=9.0

EXCITATION : MG ANALYSER MODE: FRR
SCAN MODE : T FACTOR : 0

MAGNIFICATION: L RESOLUTION: M

BASELINE THRESHOLD: 0 MIN. PEAK WIDTH: 1.00

REGION: 1 - WITH MARKERS

EUNIT	K.E.	STEP	DWELL	#CHAN	#AVG
XS	1033.60	0.10	0.200	250	10

SCAN: 1

START E.V. : 1074.80 END E.V. : 1093.50

PEAK	K.E.	B.E.	MAX	AREA	FWHH
1	1084.70	163.30	5827	181164	3.10

RUN	REG	SCAN	STEP	#CH
Y120	1	1	.10	88

ELMT	K.E.	DWELL
XS	1089.60	.200

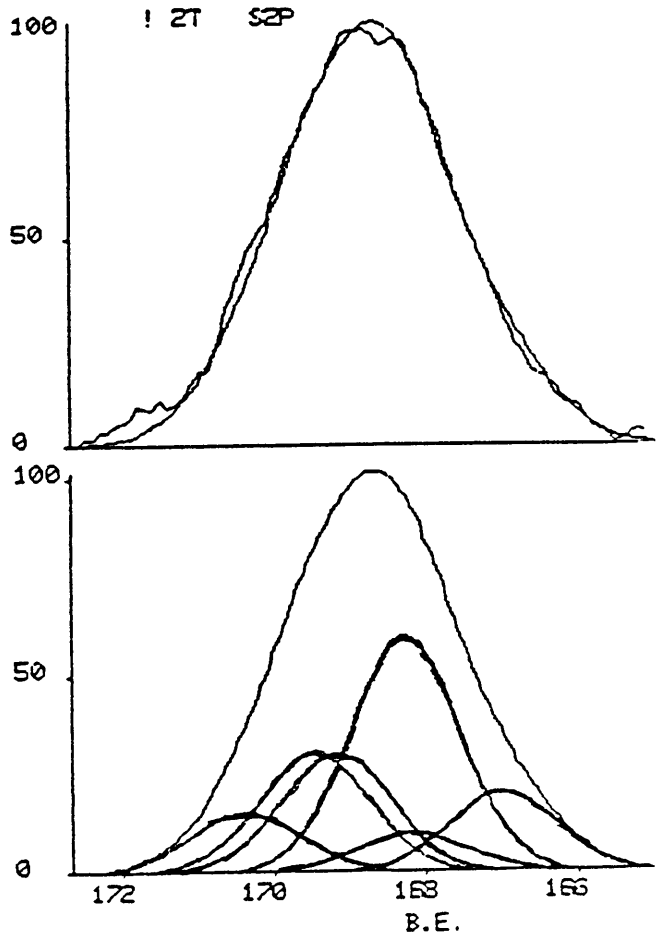
START EV: 172.70
END EV: 164.00

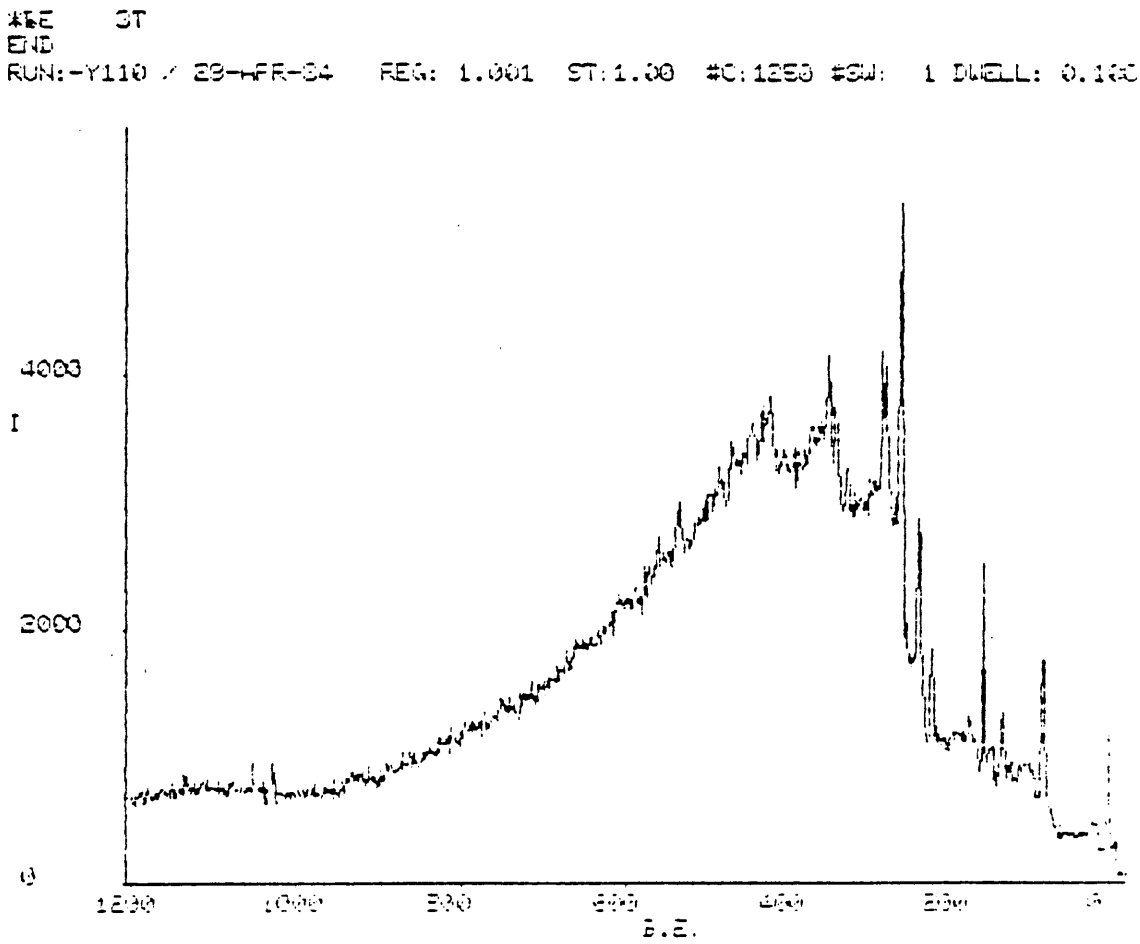
100% AREA =164644

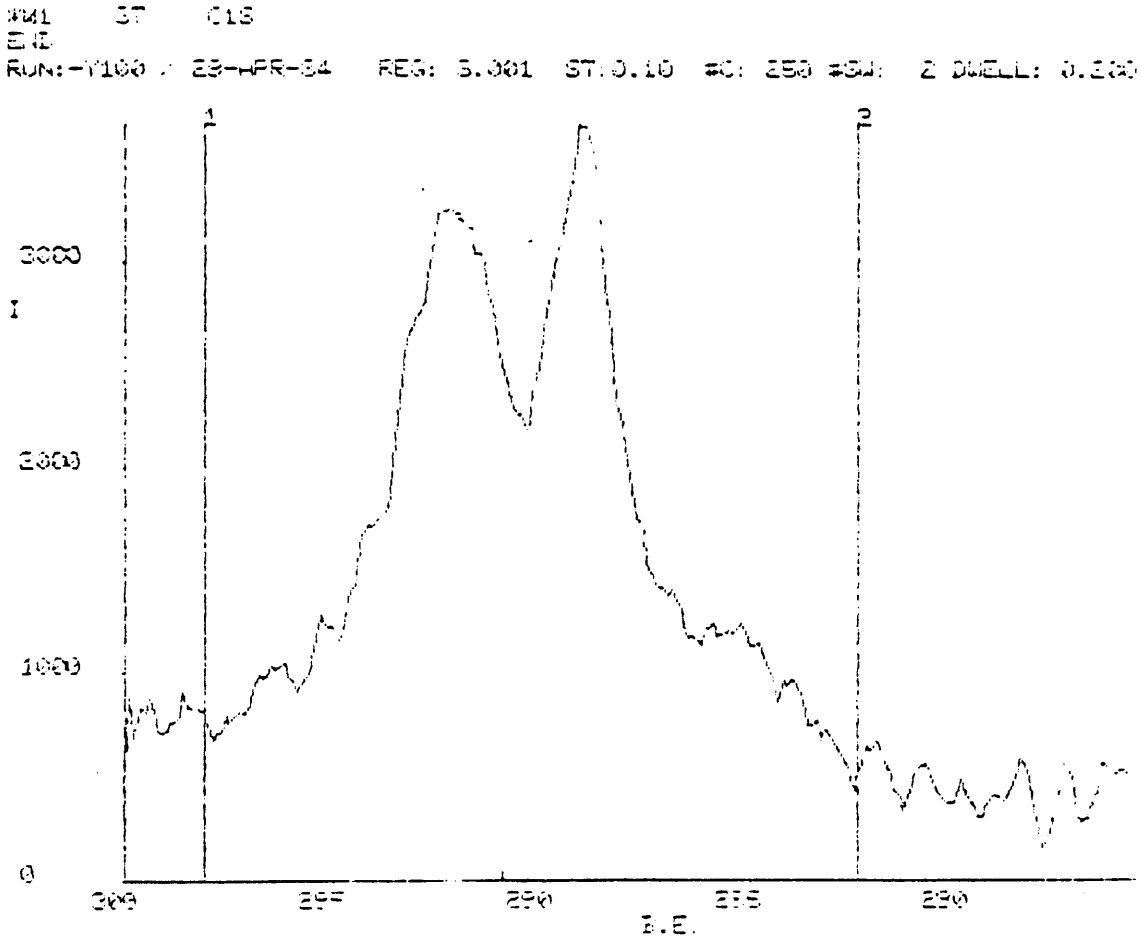
100% INTENSITY =5387

FIT=15

PK	ENERGY	MAX	FWHH	AREA
1G	170.40	15.00	1.70	8.9
2G	169.20	30.00	1.70	17.8
3G	169.50	30.00	1.70	17.8
4G	168.30	60.00	1.70	35.6
5G	168.20	10.00	1.70	5.9
6G	167.00	20.00	1.70	11.8




*GE 3T
END
RUN:-Y110 / 29-WFR-34 REG: 1.001 ST:1.00 #C:1250 #SW: 1 DWELL: 0.100
4000
I
2000
0
1200
1000
800
600
400
200
0
B.E.


001 37 C1S
E.E.
RUN:-Y100 / 23-APR-84 REG: 3.001 ST:0.10 #C: 250 #SW: 2 DWELL: 0.200
1
2
3000
I
2000
1000
0
300
295
290
285
280
B.E.

RUN : Y100 / 29-APR-84
SAMPLE: 1
NAME : 3T
TITLE : DR YOON
13KV 20MA SLIT=2 CUR=9.0

EXCITATION : MG ANALYSER MODE: FRR
SCAN MODE : T FACTOR : 0

MAGNIFICATION: L RESOLUTION: M

BASELINE THRESHOLD: 0 MIN. PEAK WIDTH: 1.00

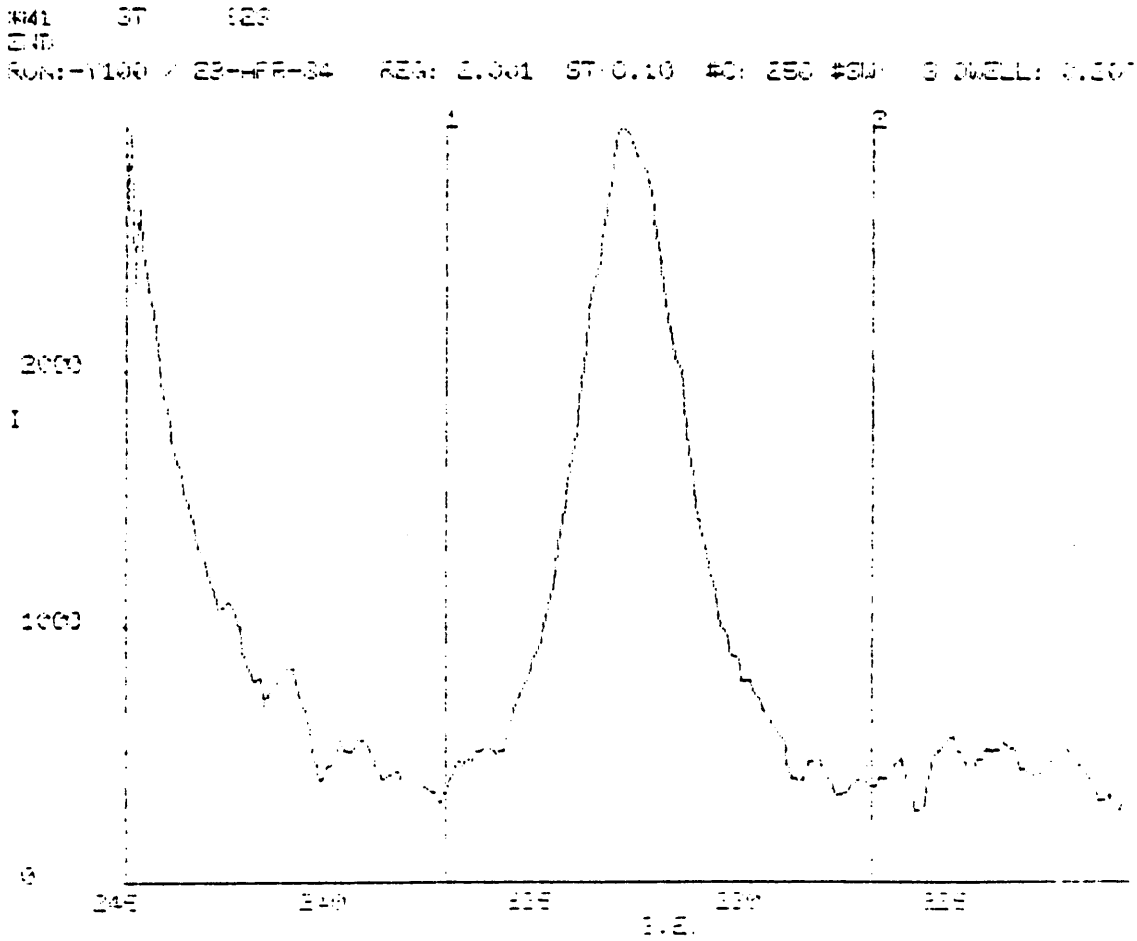
REGION: 3 - WITH MARKERS

ELMT	K.E.	STEP	DWELL	#CHAN	#AVG
XC1	963.60	0.10	0.200	250	2

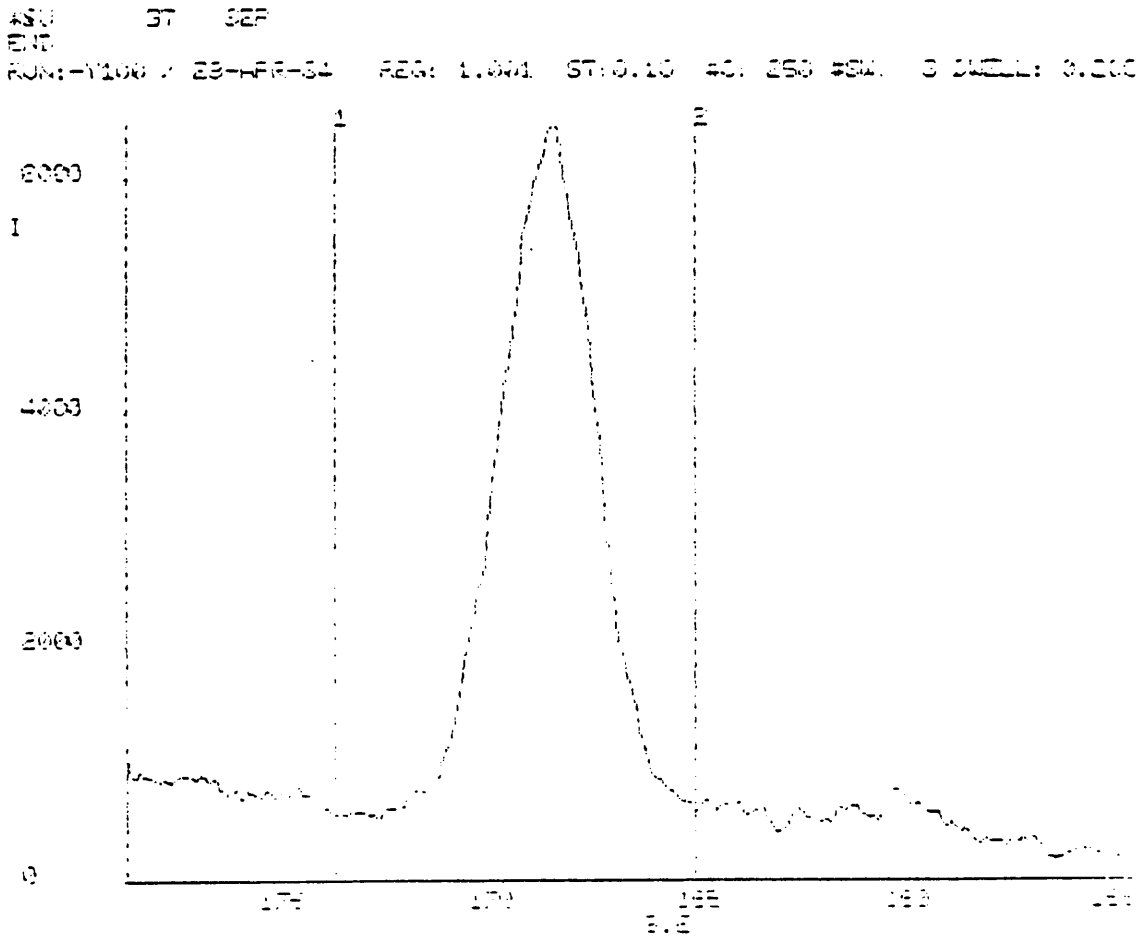
SCAN: 1

START E.V. : 953.60 END E.V. : 978.50

PEAK	K.E.	B.E.	MAX	AREA	FWHH
1	964.60	289.00	3111	180310	5.40


2000
1000
0
I
1
2
1.2.

```
RUN    : Y100 / 23-APR-84
SAMPLE:      1
NAME   : ST
TITLE  : DR YOON
         13KV 20MA SLIT=2 D.R=3.0

EXCITATION : MG            ANALYSER MODE: FRR
SCAN MODE  : T             FACTOR       :  0

MAGNIFICATION: L            RESOLUTION: M

BASELINE THRESHOLD:   0      MIN. PEAK WIDTH:  1.00


REGION:  2  -  WITH MARKERS
 ELMT      K.E.        STEP      DWELL     #CHAN    #AVG
 XS2S    1023.60       0.10      0.200      250       3

SCAN:  1

          START E.V. : 1020.60 END E.V. : 1033.50
  PEAK     K.E.        B.E            MAX        AREA        FWHM

    1    1020.60     233.00          2333       5365        2.00
```


ST SEP
RUN:-Y100 / 23-APR-84 REG: 1.001 ST:0.10 #C: 250 #SA: 3 DWELL: 0.200
1
2
6000
I
4000
2000
0
175
170
165
160
155
3.2

```
RUN   : Y100 / 29-APR-84
SAMPLE:      1
NAME  : ST
TITLE : DR YOON
        15KV 20MA SLIT=2 CLR=3.0

EXCITATION : MG          ANALYSER MODE: FRR
SCAN MODE  : T           FACTOR       : 0

MAGNIFICATION: L          RESOLUTION: M

BASELINE THRESHOLD:   0     MIN. PEAK WIDTH:  1.00


REGION:  1  -  WITH MARKERS
 ELMT     K.E.        STEP      DWELL     #SCAN    #AVG
 XS     1039.60       0.10      0.200      250       3

SCAN:  1

          START E.V. : 1074.60 END E.V  : 1039.50
  PEAK    K.E.        B.E.          MAX       AREA       FWHM

    1   1084.30     123.00         3337     158913       2.10
```

RUN	REG	SCAN	STEP	#CH
Y100	1	1	.10	86

ELMT	K.E.	DWELL
XS	1089.60	.200

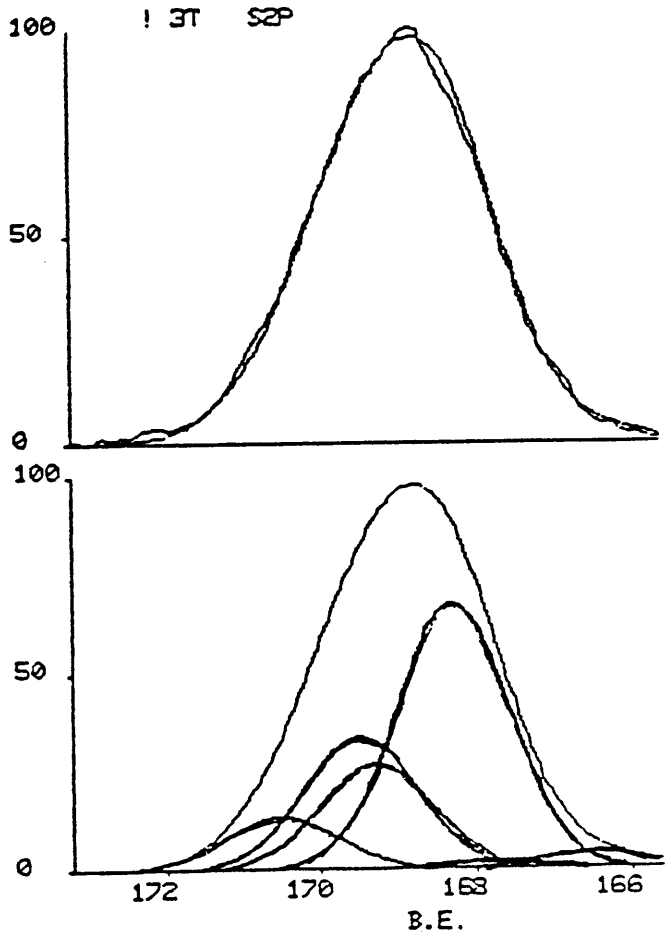
START EV: 173.20
END EV: 164.70

100% AREA =157937

100% INTENSITY =5878

FIT=7

PK	ENERGY	MAX	FWHH	AREA
1G	170.50	13.50	1.70	9.1
2G	169.30	27.00	1.70	18.2
3G	169.50	34.00	1.70	22.9
4G	168.30	68.00	1.70	45.9
5G	167.70	2.00	1.70	1.3
6G	166.50	4.00	1.70	2.6



RUN	REG	SCAN	STEP	#CH
Y100	1	1	.10	86

ELMT	K.E.	DWELL
XS	1089.60	.200

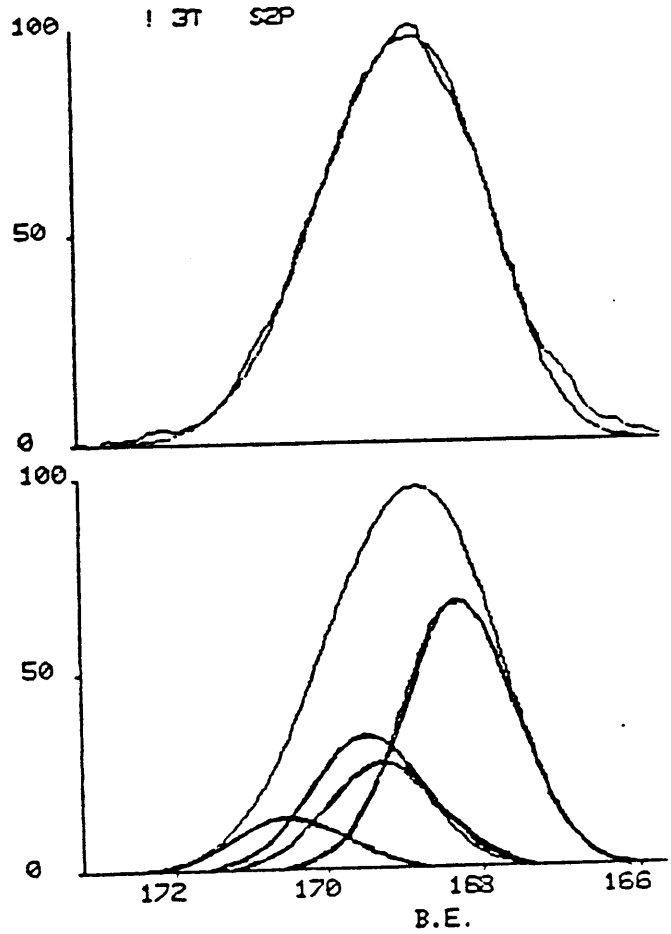
START EV: 173.20
END EV: 164.70

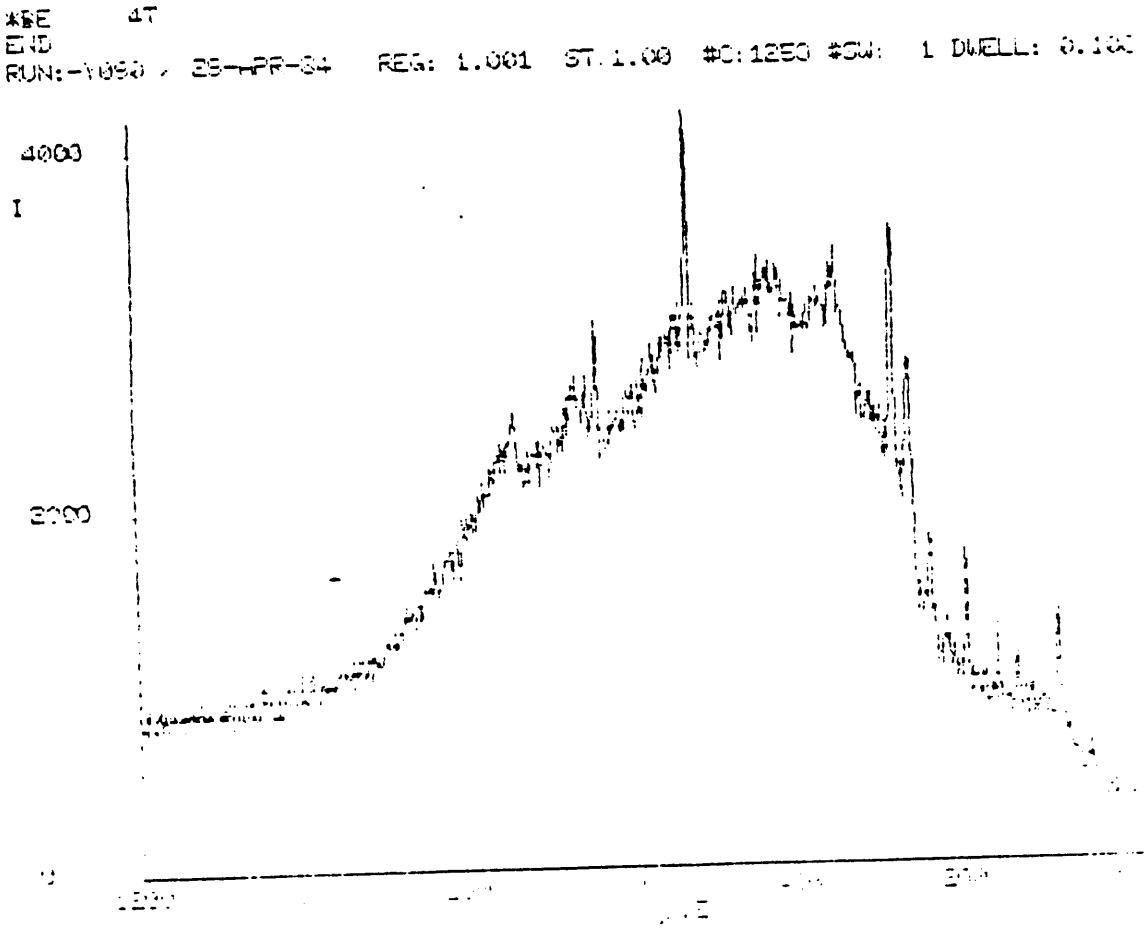
100% AREA =157937

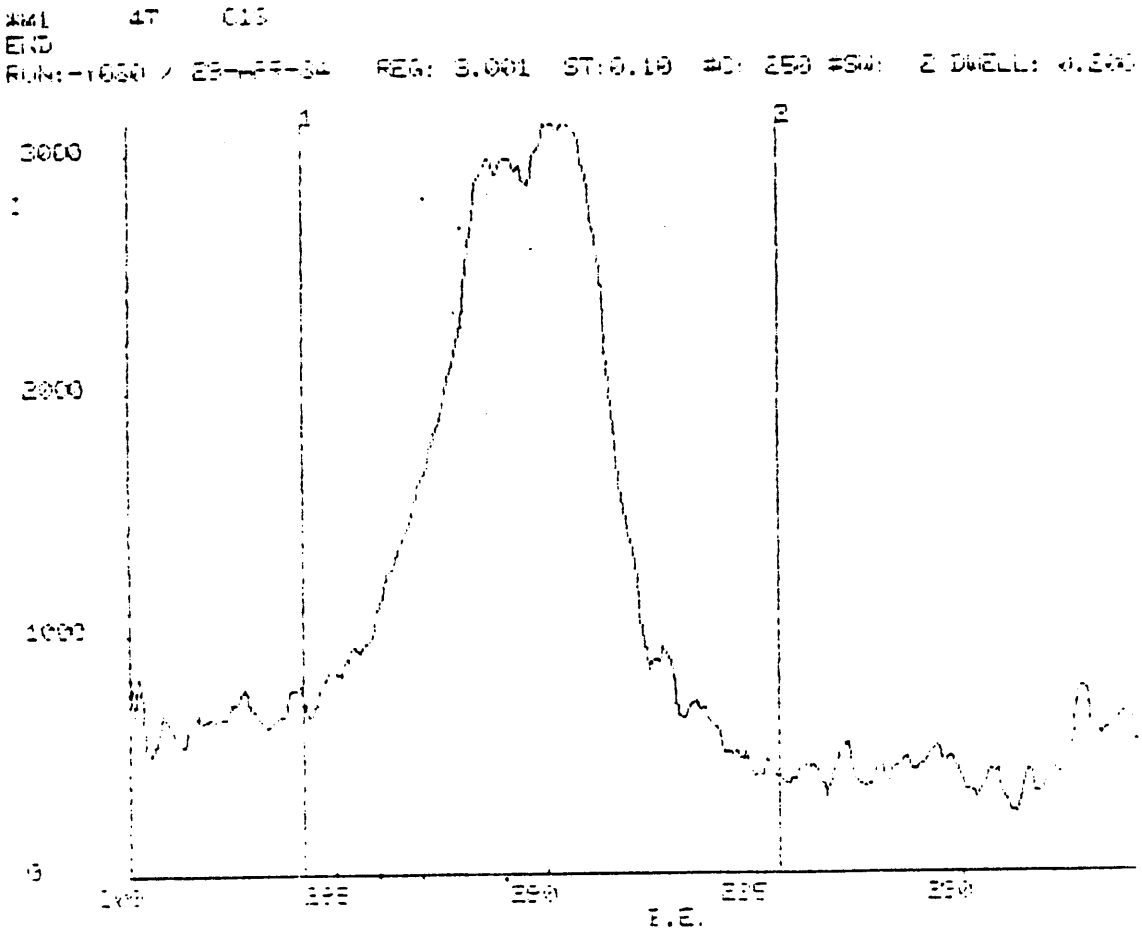
100% INTENSITY =5878

FIT=11

PK	ENERGY	MAX	FWHH	AREA
1G	170.50	13.50	1.70	9.1
2G	169.30	27.00	1.70	18.2
3G	169.50	34.00	1.70	22.9
4G	168.30	68.00	1.70	45.9




*BE 4T
END
RUN:-1090 , 25-APR-84 REG: 1.001 ST.1.00 #C:1250 #SW: 1 DWELL: 0.10
4000
I
3000


AM1 47 C13
END
RUN:-1680 / 23-FF-34 REG: 3.001 ST:0.10 #D: 250 #SW: 2 DWELL: 0.240
1
2
3000
2000
1000
0
100
150
200
250
300
E.E.

RUN : YOOO / 23-APR-84
SAMPLE: 1
NAME : LT
TITLE : DR YOON
13KV 20MA SLIT=2 CUR=3.0

EXCITATION : MG ANALYSER MODE: FRR
SCAN MODE : T FACTOR : 0

MAGNIFICATION: L RESOLUTION: M

BASELINE THRESHOLD: 0 MIN. PEAK WIDTH: 1.00

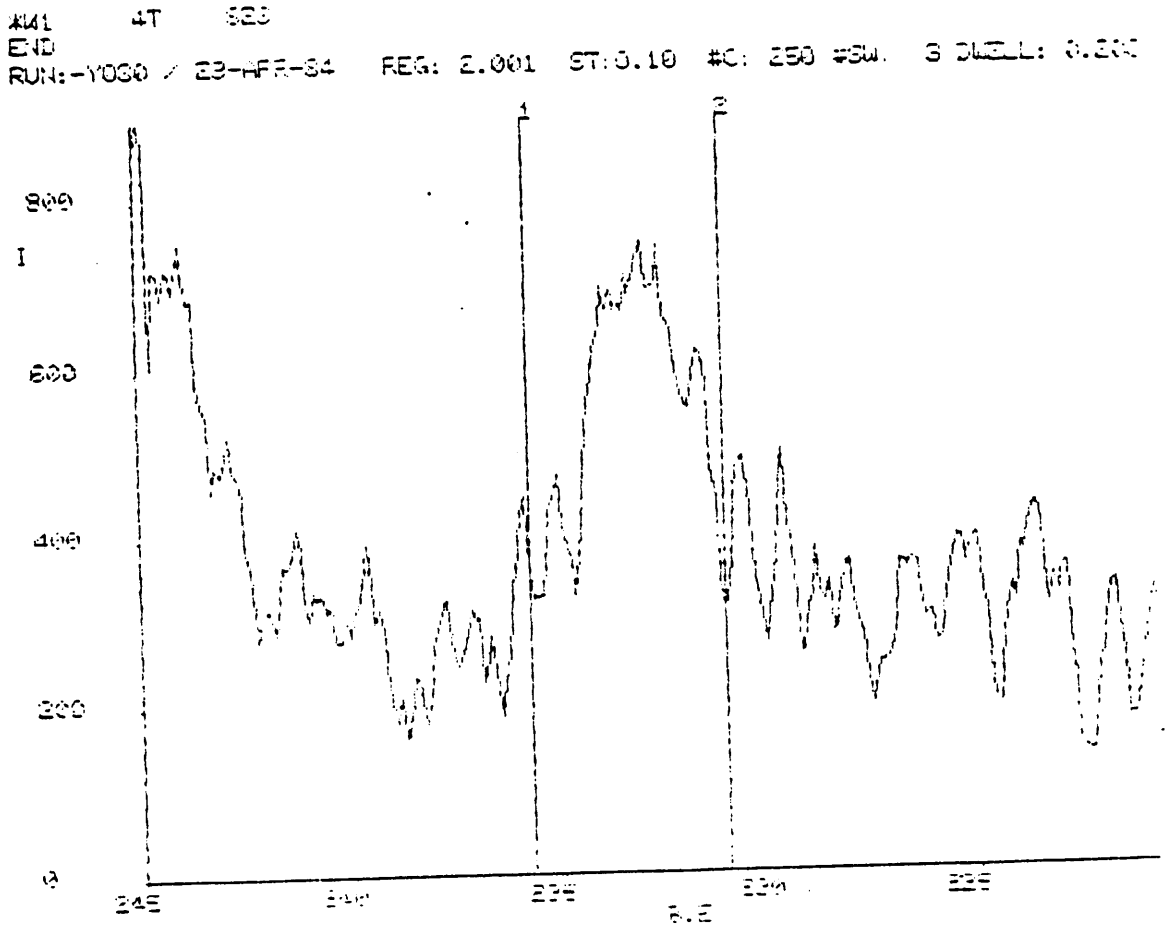
REGION: 3 - WITH MARKERS

ELMT	K.E.	STEP	DWELL	#CHAN	#AVG
XC1	583.80	0.10	0.200	250	2

SCAN: 1

START E.V. : 583.60 END E.V. : 978.50

PEAK	K.E.	B.E.	MAX	AREA	FWHH
1	584.20	283.40	2827	121540	4.10


#01 4T 523
END
RUN:-Y030 / 23-APR-84 REG: 2.001 ST:0.10 #C: 250 #SW. 3 DWELL: 0.200
1
2
800
I
600
400
200
0
245
240
235
230
225
E.E

RUN : Y060 / 23-APR-84
SAMPLE: 1
NAME : 4T
TITLE : IR YOON
13KV 20MA SLIT=2 CUR=8.0

EXCITATION : MG ANALYSER MODE: FRR
SCAN MODE : T FACTOR : 0

MAGNIFICATION: L RESOLUTION: M

BASELINE THRESHOLD: 0 MIN. PEAK WIDTH: 1.00

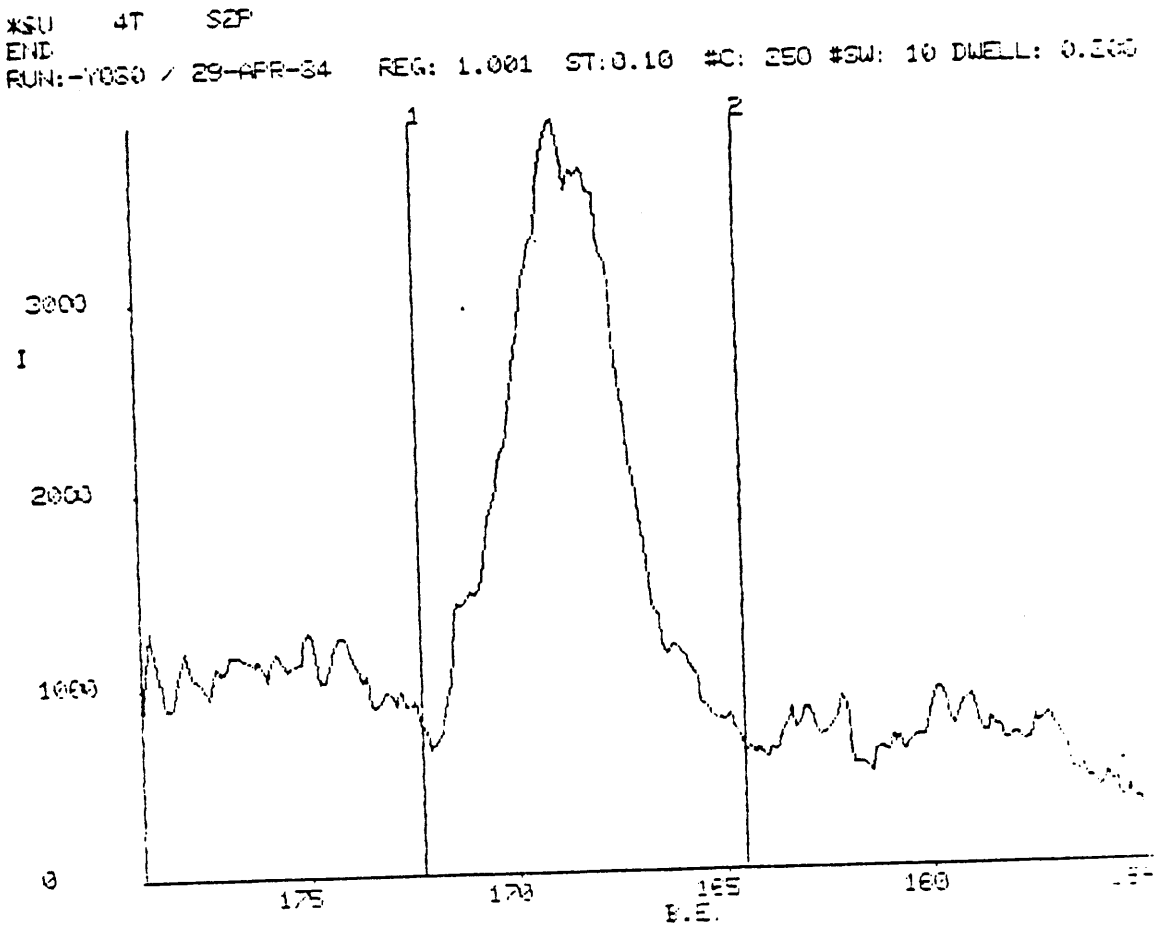
REGION: 2 - WITH MARKERS

ELMT	K.E.	STEP	DWELL	#CHAN	#AVG
XGZS	1023.60	0.10	0.200	250	3

SCAN: 1

START E.V. : 1000.60 END E.V. : 1033.50

PEAK	K.E.	B.E.	HAA	AREA	FWHH
1	1020.60	230.00	333	10337	3.00


*SU 4T S2P
END
RUN:-Y030 / 29-APR-84 REG: 1.001 ST:0.10 #C: 250 #SW: 10 DWELL: 0.200
1
2
3000
I
2000
1000
0
175
170
165
160
B.E.

RUN : 7030 / 29-APR-84
SAMPLE: 1
NAME : 4T
TITLE : IR YOON
13KV 20MA SLIT=2 CUR=8.0

EXCITATION : MG ANALYSER MODE: FRR
SCAN MODE : T FACTOR : 0

MAGNIFICATION: L RESOLUTION: M

BASELINE THRESHOLD: 0 MIN. PEAK WIDTH: 1.00

REGION: 1 - WITH MARKERS

ELMT	K.E.	STEP	DWELL	#CHAN	#AVG
XS	1038.80	0.10	0.200	250	10

SCAN: 1

START E.V. : 1074.80 END E.V. : 1038.50

PEAK	K.E.	B.E.	MAX	AREA	FWHH
1	1034.80	168.00	3213	102764	2.30

RUN	REG	SCAN	STEP	#CH
Y080	1	1	.10	85

ELMT	K.E.	DWELL
XS	1089.60	.200

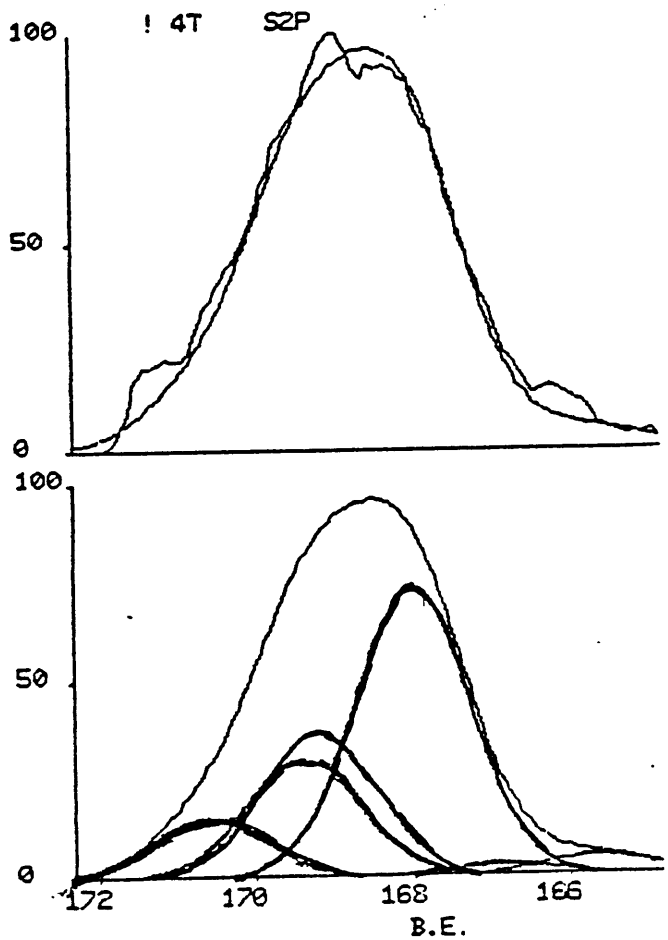
START EV: 172.30
END EV: 163.90

100% AREA =99424

100% INTENSITY =3201

FIT=39

PK	ENERGY	MAX	FWHH	AREA
1G	170.60	15.00	1.70	8.6
2G	169.40	30.00	1.70	17.5
3G	169.20	37.00	1.70	21.6
4G	168.00	74.00	1.70	43.2
5G	165.60	5.00	1.70	2.9
6G	166.80	2.50	1.70	1.4



RUN	REG	SCAN	STEP	#CH
Y080	1	1	.10	94

ELMT	K.E.	DWELL
XS	1089.60	.200

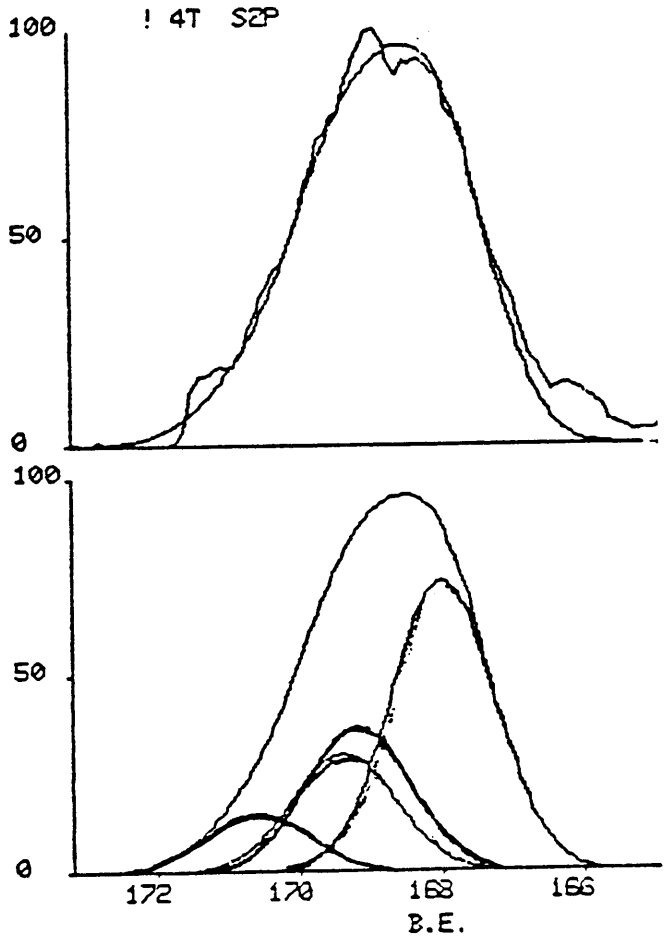
START EV: 173.20
END EV: 163.90

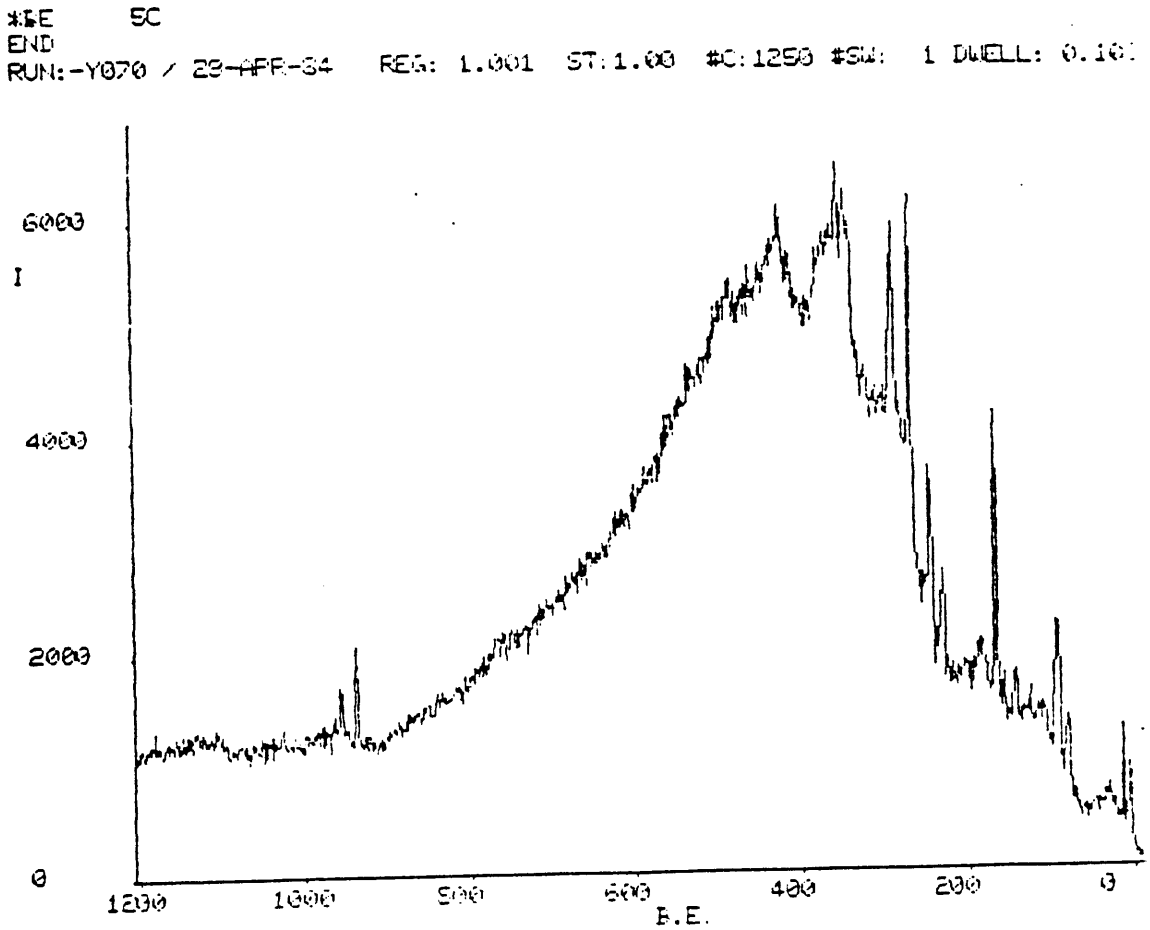
100% AREA =94822

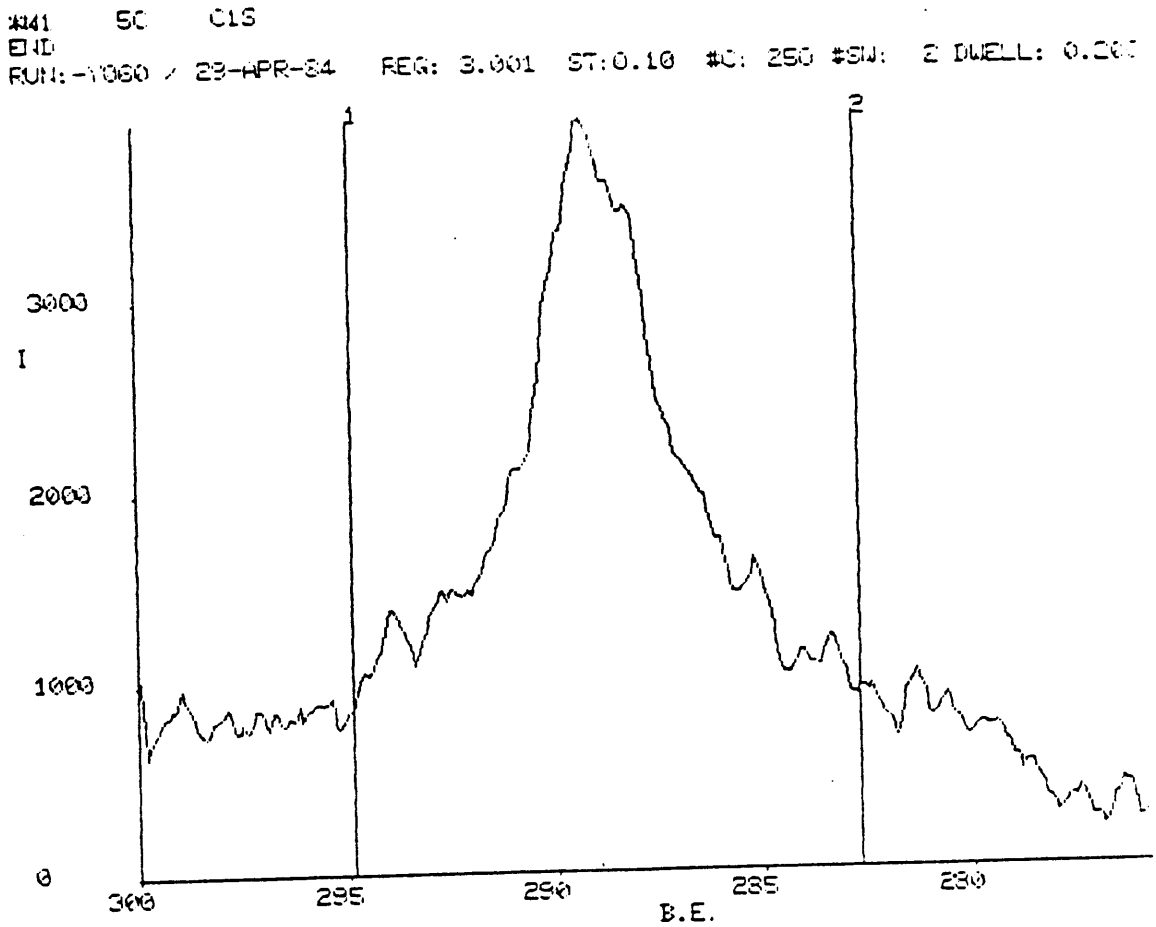
100% INTENSITY =3124

FIT=49

PK	ENERGY	MAX	FWHH	AREA
1G	170.60	15.00	1.70	8.9
2G	169.40	30.00	1.70	17.9
3G	169.20	37.00	1.70	22.1
4G	168.00	74.00	1.70	44.2




*SE 5C
END
RUN:-Y070 / 29-APR-84 REG: 1.001 ST:1.00 #C:1250 #SW: 1 DWELL: 0.10
6000
I
4000
2000
0
1200
1000
800
600
400
200
0
B.E.


#41 5C C1S
END
RUN:-1060 / 23-APR-84 REG: 3.001 ST:0.10 #C: 250 #SW: 2 DWELL: 0.20
1
2
3000
I
2000
1000
0
300
295
290
285
280
B.E.

RUN : Y060 / 29-APR-84
SAMPLE: 1
NAME : SC
TITLE : DR YOON
13KV 20MA SLIT=2 CUR=3.0

EXCITATION : MG ANALYSER MODE: FRR
SCAN MODE : T FACTOR : 0

MAGNIFICATION: L RESOLUTION: M

BASELINE THRESHOLD: 0 MIN. PEAK WIDTH: 1.00

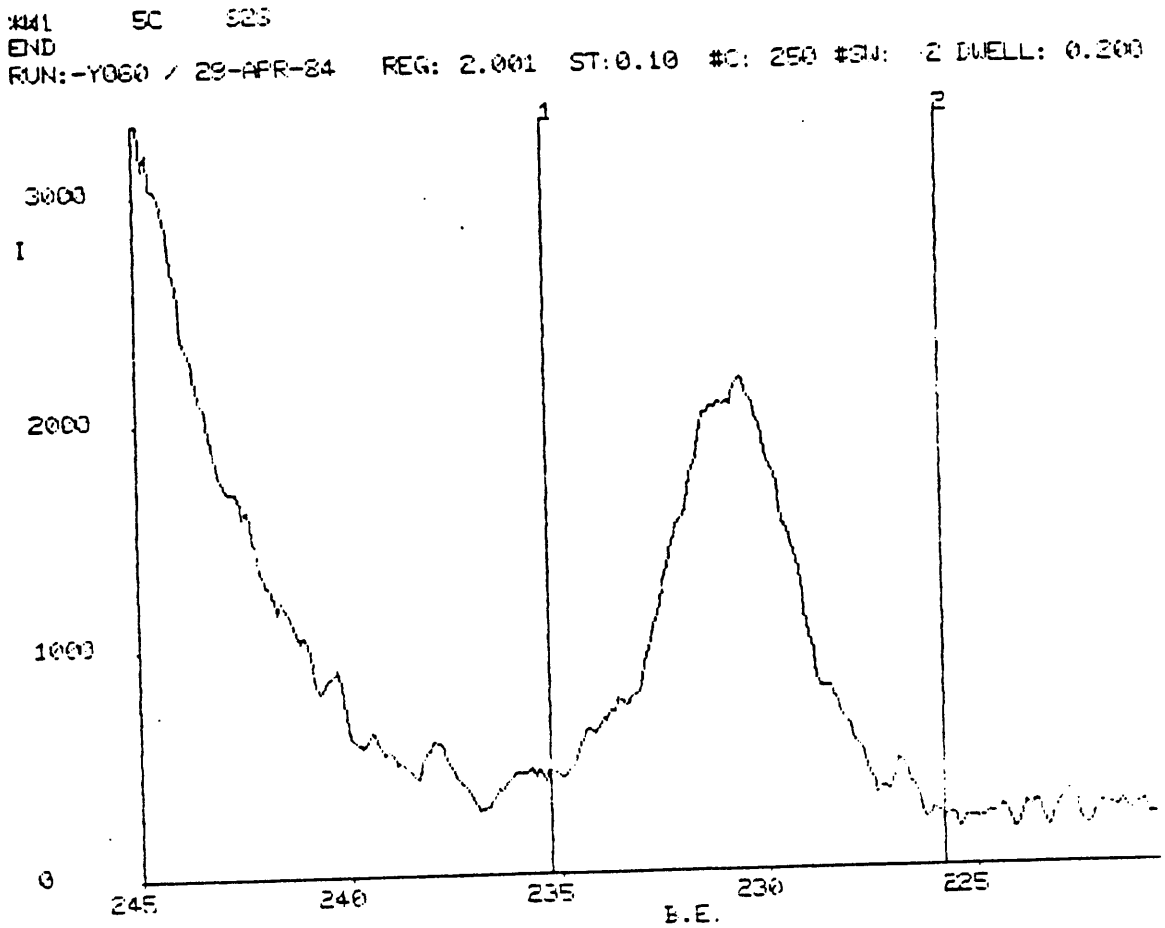
REGION: 3 - WITH MARKERS

ELMT	K.E.	STEP	DWELL	#CHAN	#AVG
XC1	968.60	0.10	0.200	250	2

SCAN: 1

START E.V. : 953.60 END E.V. : 978.50

PEAK	K.E.	B.E.	MAX	AREA	FWHH
1	984.30	289.30	3019	127276	3.00


XM1 SC 525
END
RUN:-Y060 / 29-APR-84 REG: 2.001 ST:0.10 #C: 250 #SW: 2 DWELL: 0.200
1
2
3000
I
2000
1000
0
245
240
235
230
225
B.E.

RUN : Y060 / 29-APR-84
SAMPLE: 1
NAME : 5C
TITLE : DR YOON
13KV 20MA SLIT=2 CUR=9.0

EXCITATION : MG ANALYSER MODE: FRR
SCAN MODE : T FACTOR : 0

MAGNIFICATION: L RESOLUTION: M

BASELINE THRESHOLD: 0 MIN. PEAK WIDTH: 1.00

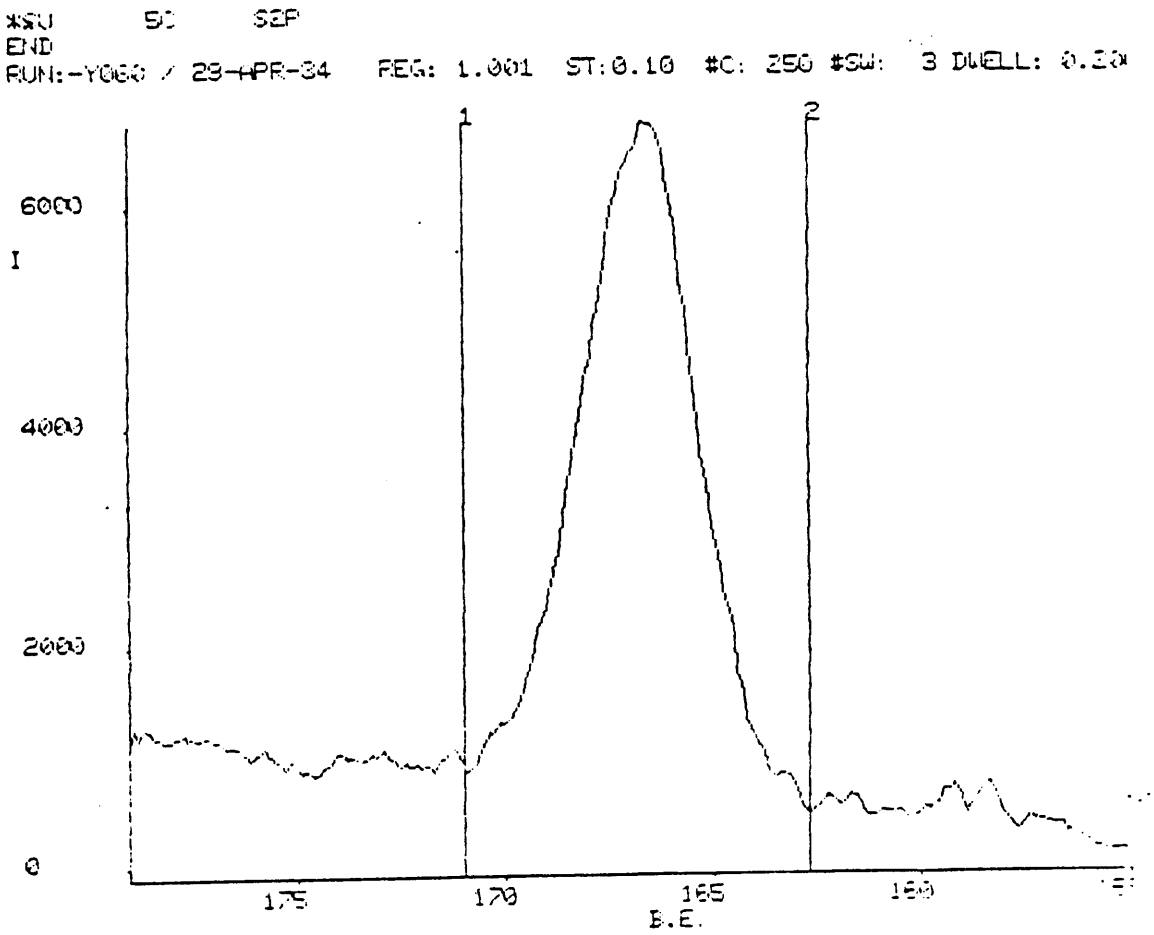
REGION: 2 - WITH MARKERS

ELMT	K.E.	STEP	DWELL	#CHAN	#AVG
XS2S	1023.60	0.10	0.200	250	2

SCAN: 1

START E.V. : 1008.60 END E.V. : 1033.50

PEAK	K.E.	B.E.	MAX	AREA	FWHH
1	1023.10	230.50	1323	66178	3.30


*SU 5C S2P
END
RUN:-Y060 / 23-APR-84 REG: 1.001 ST:0.10 #C: 250 #SW: 3 DWELL: 0.30
1
2
6000
I
4000
2000
0
175
170
165
160
B.E.

RUN : Y060 / 23-APR-84
SAMPLE: 1
NAME : 5C
TITLE : DR YOON
13KV 20MA SLIT=2 CUR=9.0

EXCITATION : MG ANALYSER MODE: FRR
SCAN MODE : T FACTOR : 0

MAGNIFICATION: L RESOLUTION: M

BASELINE THRESHOLD: 0 MIN. PEAK WIDTH: 1.00

REGION: 1 - WITH MARKERS

ELMT	K.E.	STEP	DWELL	#CHAN	#AVG
XS	1089.60	0.10	0.200	250	3

SCAN: 1

START E.V. : 1074.60 END E.V. : 1099.50

PEAK	K.E.	B.E.	MAX	AREA	FWHH
1	1037.10	166.50	6106	204353	3.10

FIL.	REG	SCAN	STEP	#CH
0000	1	1	.10	33

EXCIT	K.E.	DWELL
MG	1089.00	.200

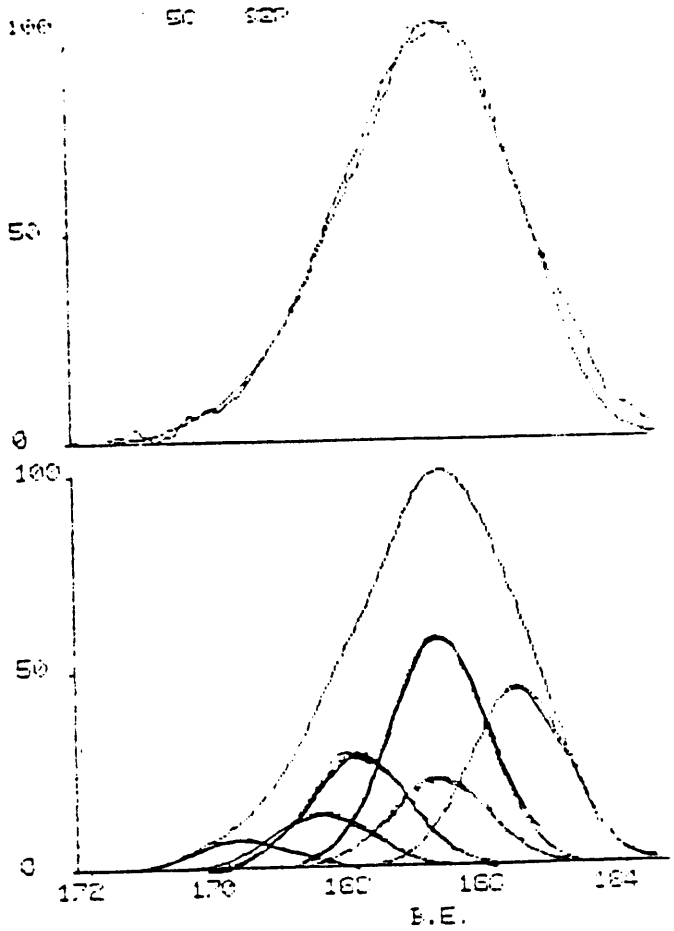
START EV: 172.20
END EV: 182.40

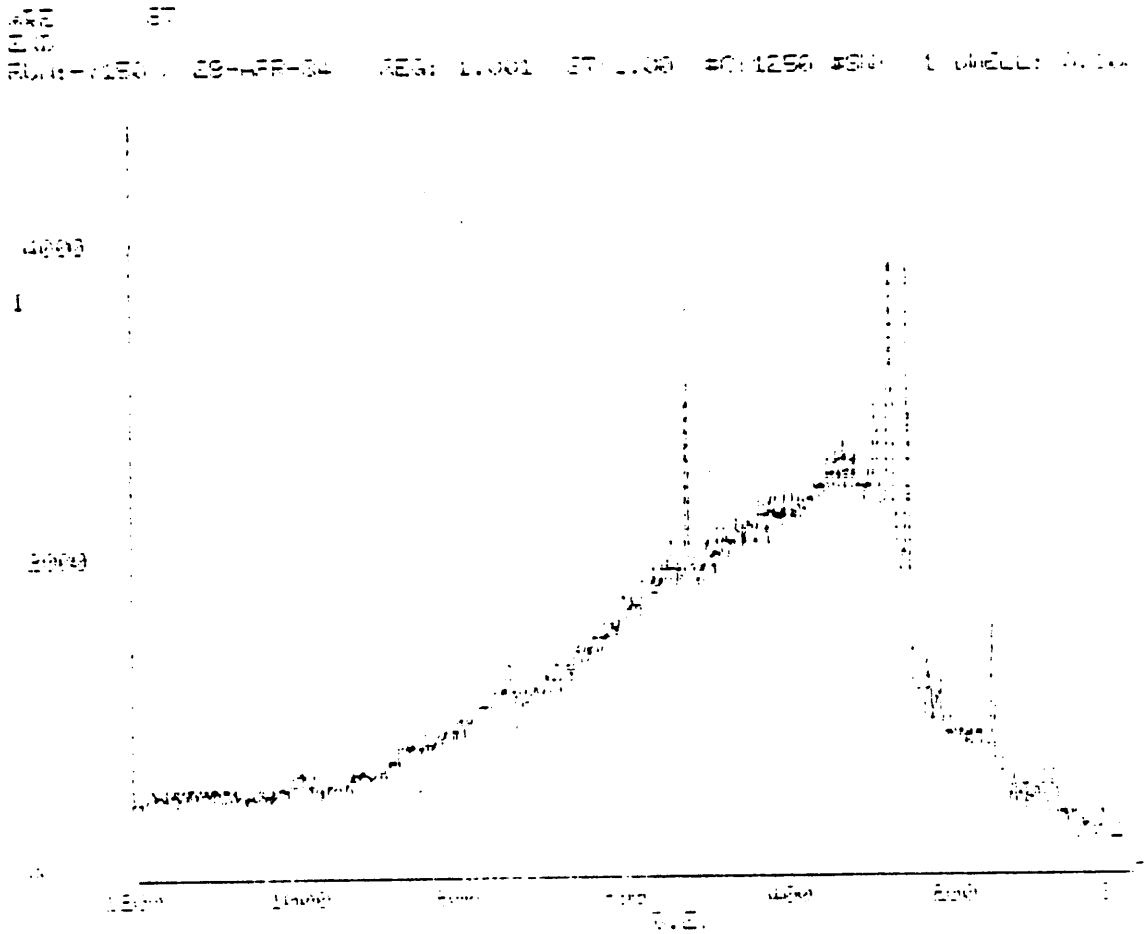
100% AREA =201351

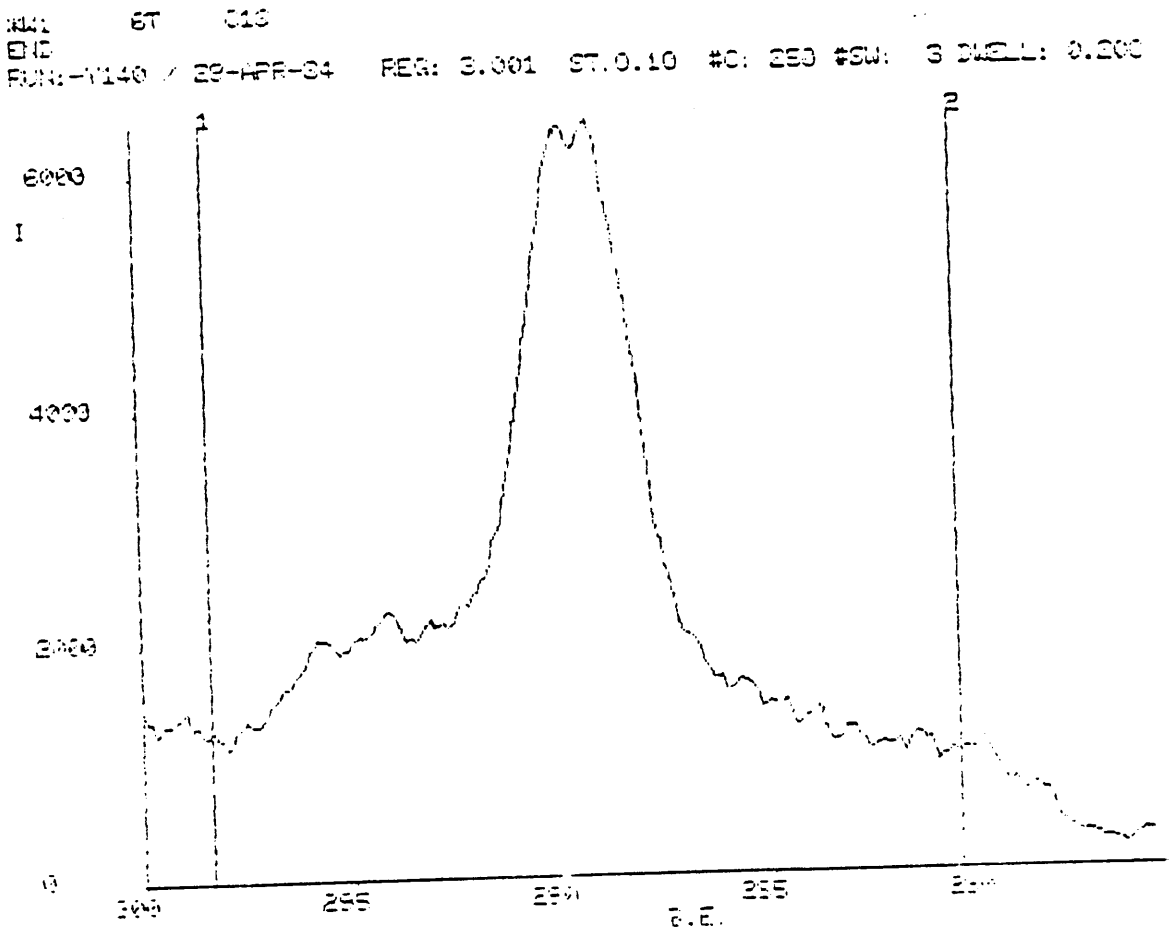
100% INTENSITY =6042

FIT=18

PK	ENERGY	MAX	FWHH	AREA
1G	168.70	7.00	1.70	3.8
2G	168.50	14.00	1.70	7.6
3G	168.00	29.00	1.70	15.7
4G	166.50	58.00	1.70	31.5
5G	166.00	22.50	1.70	12.2
6G	165.00	45.00	1.70	24.5






6000
I
4000
2000
0
1
2
295
B.E.

RUN : Y140 / 29-APR-84
SAMPLE: 1
NAME : 6T
TITLE : DR YOON
15KV 20MA SLIT=2 CUR=3.0

EXCITATION : MG ANALYSER MODE: TRR
SCAN MODE : T FACTOR : 0

MAGNIFICATION: L RESOLUTION: M

BASELINE THRESHOLD: 0 MIN. PEAK WIDTH: 1.00

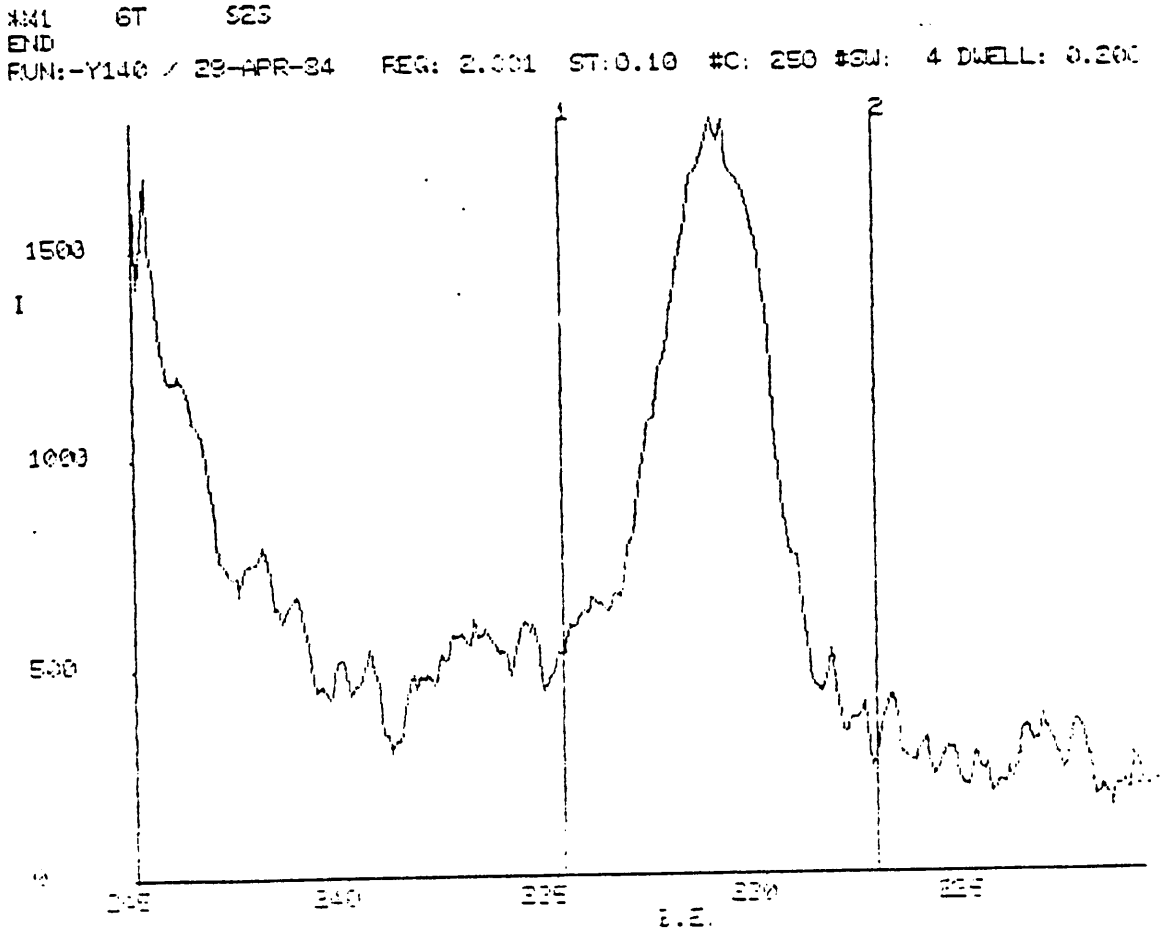
REGION: 3 - WITH MARKERS

ELMT	K.E.	STEP	DWELL	#CHAN	#AVG
XC1	568.60	0.10	0.200	250	3

SCAN: 1

START E.V. : 553.60 END E.V : 978.50

PEAK	K.E.	B.E.	MAX	AREA	FWHM
1	534.40	355.20	5354	240944	3.10


*X1 6T 523
END
RUN:-Y140 / 29-APR-84 FEG: 2.001 ST:0.10 #C: 250 #SW: 4 DWELL: 0.200
1
2
1500
I
1000
500
0
345
340
335
330
325
E.E.

RUN : Y140 / 23-APR-84
SAMPLE: 1
NAME : 6T
TITLE : IR YOON
13KV 20MA SLIT=E CUR=3.0

EXCITATION : MG
SCAN MODE : T

ANALYSER MODE: FRR
FACTOR : 0

MAGNIFICATION: L

RESOLUTION: M

BASELINE THRESHOLD: 0

MIN. PEAK WIDTH: 1.00

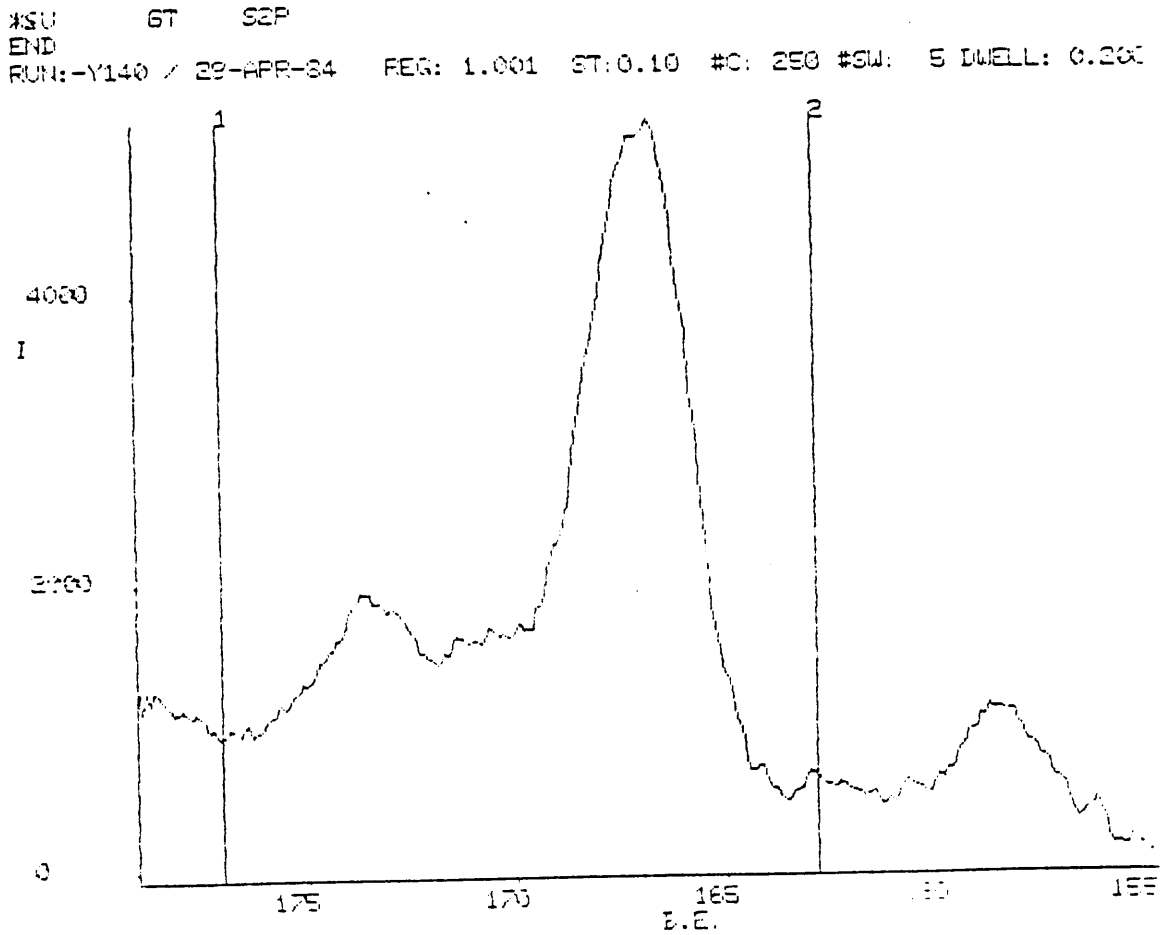
REGION: 2 - WITH MARKERS

ELMT	K.E.	STEP	DWELL	#CHAN	#AVG
XS2S	1023.60	0.10	0.200	250	4

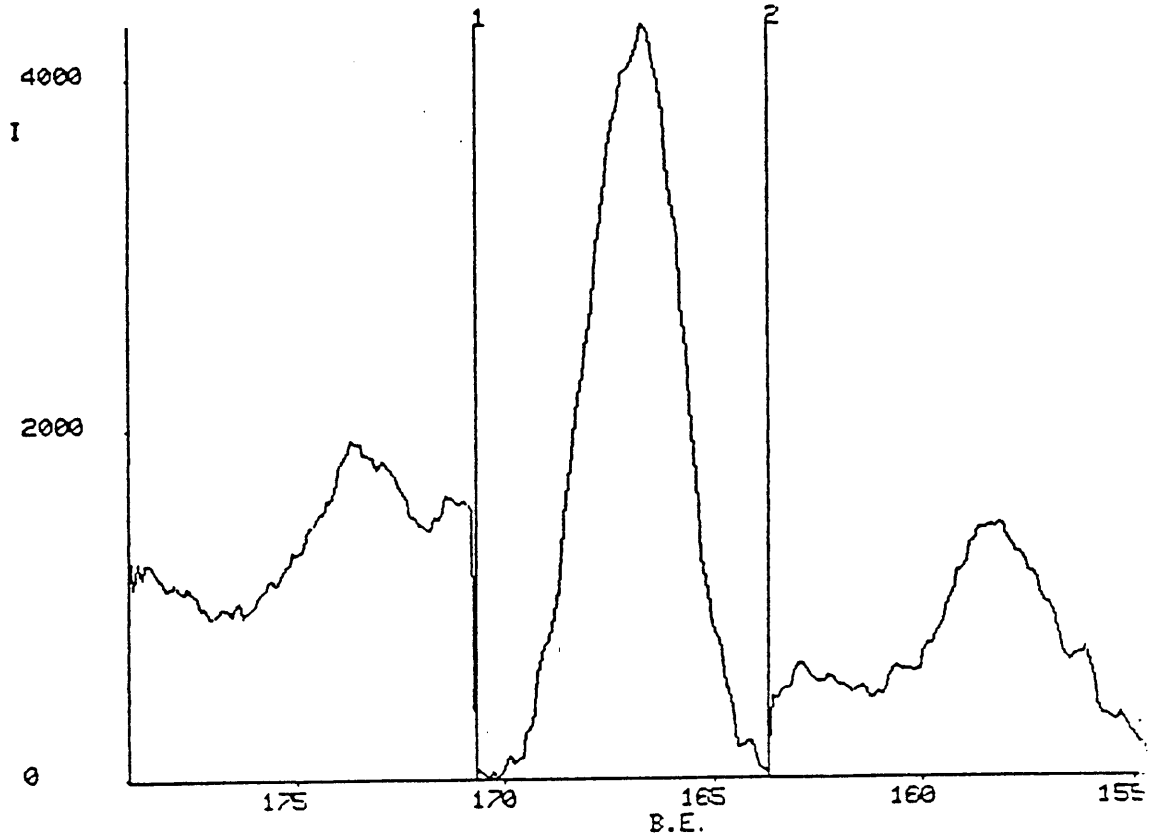
SCAN: 1

START E.V. : 1003.60 END E.V. : 1033.50

PEAK	K.E.	B.E.	MAX	AREA	FWHH
1	1022.50	231.10	1374	42339	2.30


*SU GT S2P
END
RUN:-Y140 / 29-APR-84 REG: 1.001 ST:0.10 #C: 250 #SW: 5 DWELL: 0.20
1
2
4000
I
2000
0
175
170
165
B.E.

*RE 6T S2P
END
RUN:-Y140 / 29-APR-84 REG: 1.001 ST:0.10 #C: 250 #SW: 5 DWELL: 0.200



RUN : Y140 / 29-APR-84
SAMPLE: 1
NAME : 6T
TITLE : DR YOON
13KV 20MA SLIT=2 CUR=3.0

EXCITATION : MG ANALYSER MODE: FRR
SCAN MODE : T FACTOR : 0

MAGNIFICATION: L RESOLUTION: M

BASELINE THRESHOLD: 0 MIN. PEAK WIDTH: 1.00

REGION: 1 - WITH MARKERS

ELMT	K.E.	STEP	DWELL	#CHAN	#AVG
XS	1088.60	0.10	0.200	250	5

SCAN: 1

START E.V. : 1074.60 END E.V. : 1088.50

PEAK	K.E.	B.E.	MAX	AREA	FWHM
1	1086.90	163.70	4565	182431	2.30

RUN	REG	SCAN	STEP	#CH
Y140	1	1	.10	71

ELMT	K.E.	DWELL
XS	1089.60	.200

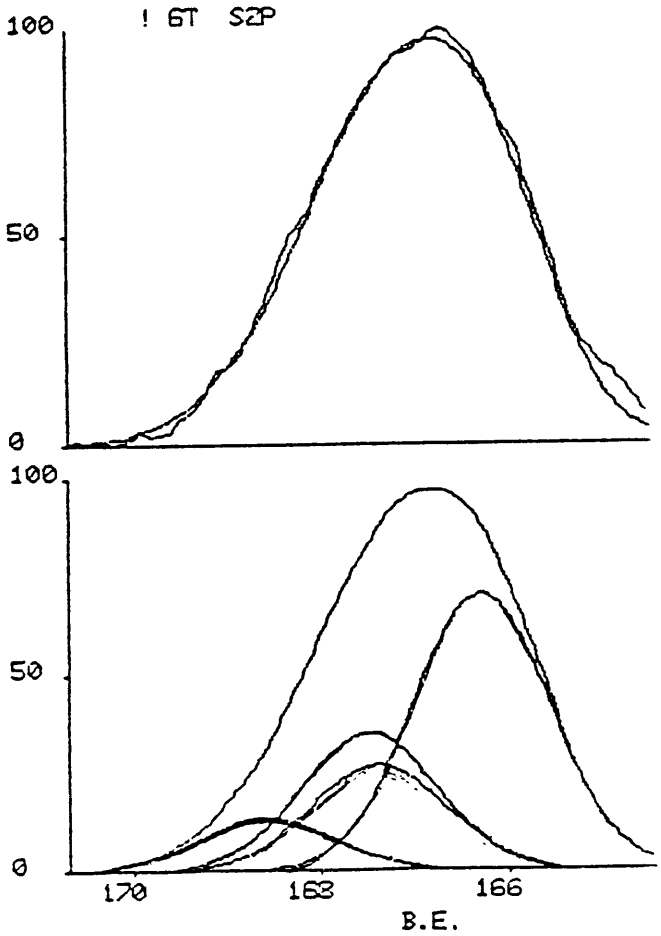
START EV: 170.70
END EV: 163.70

100% AREA =118503

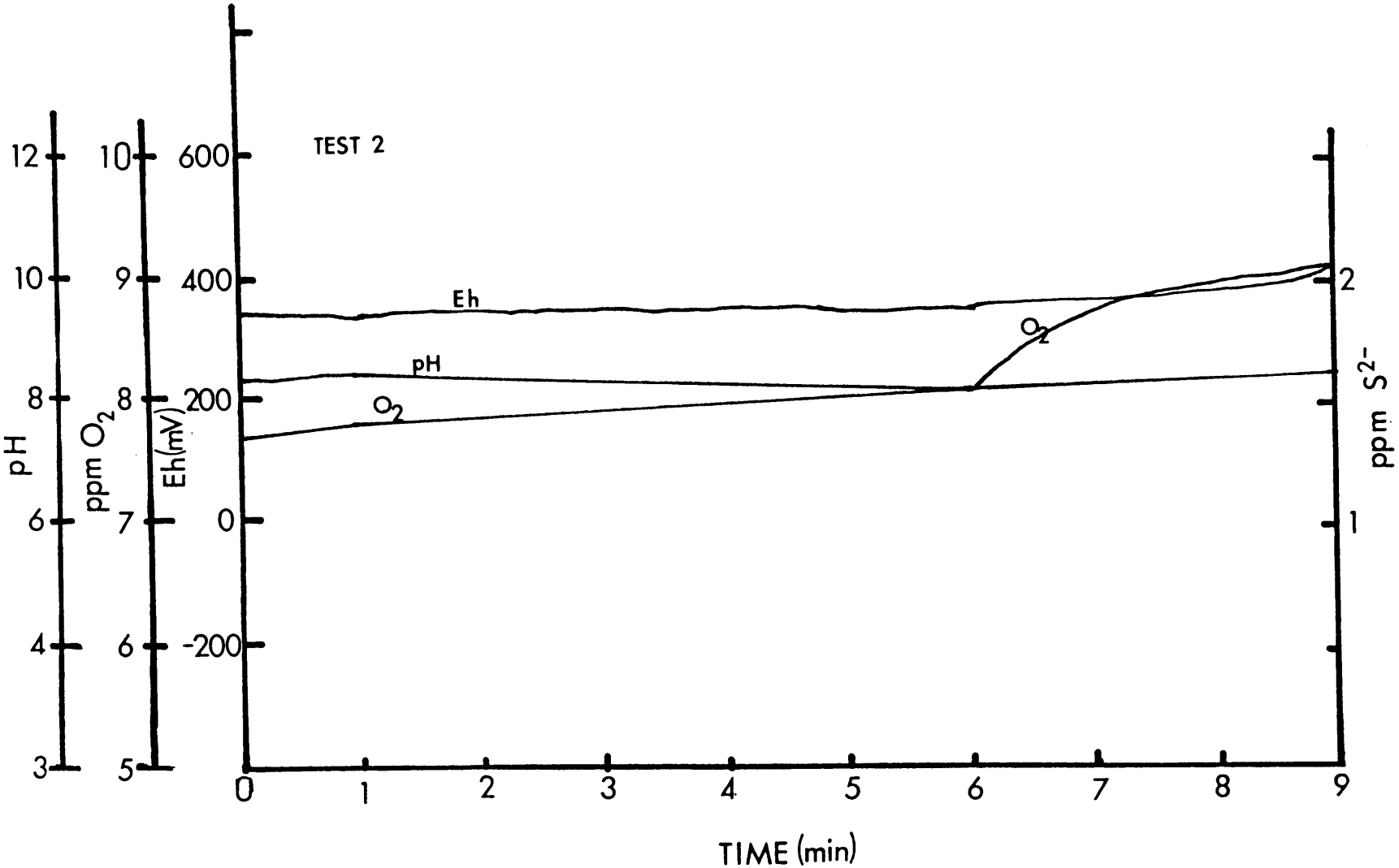
100% INTENSITY =4306

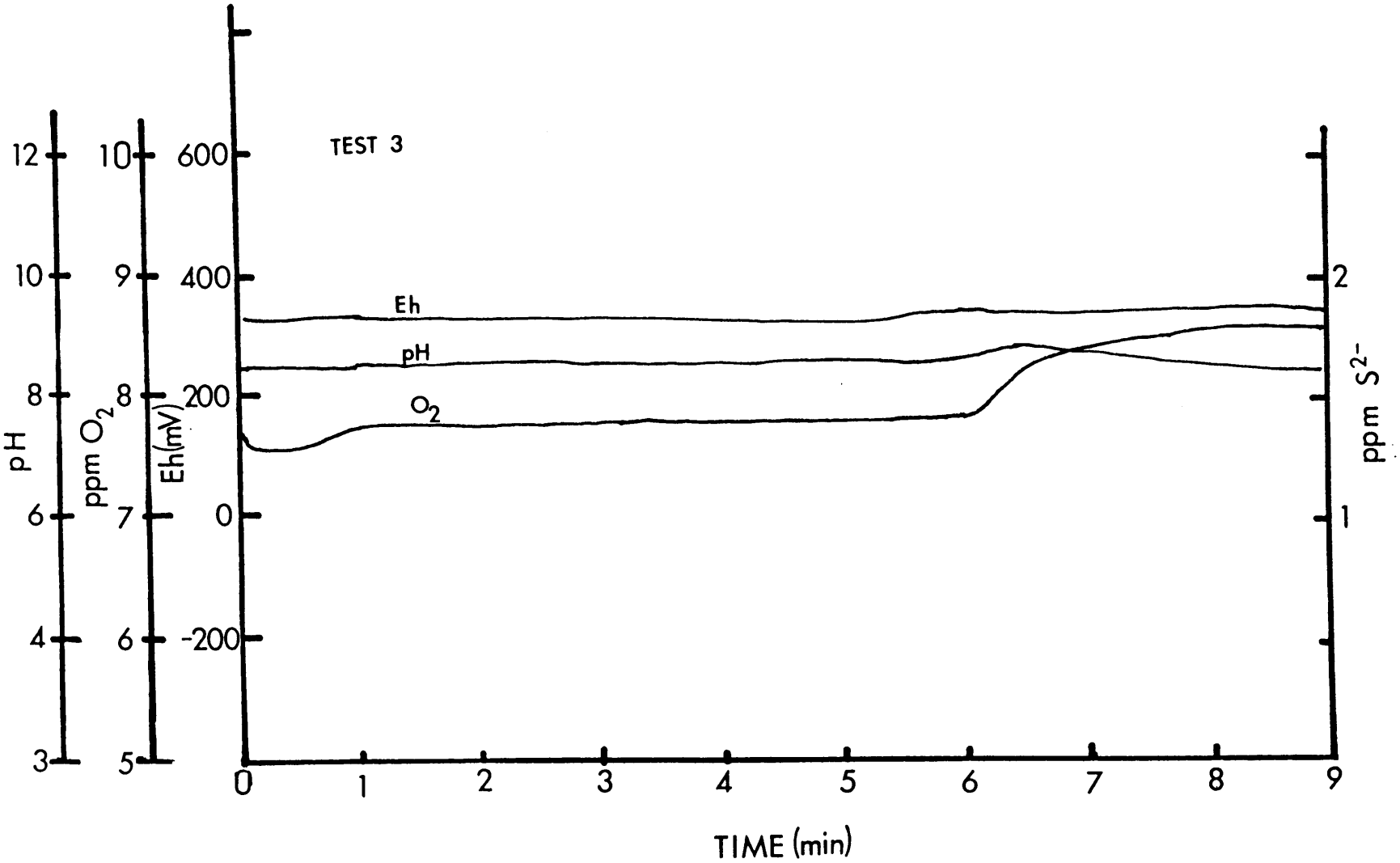
FIT=17

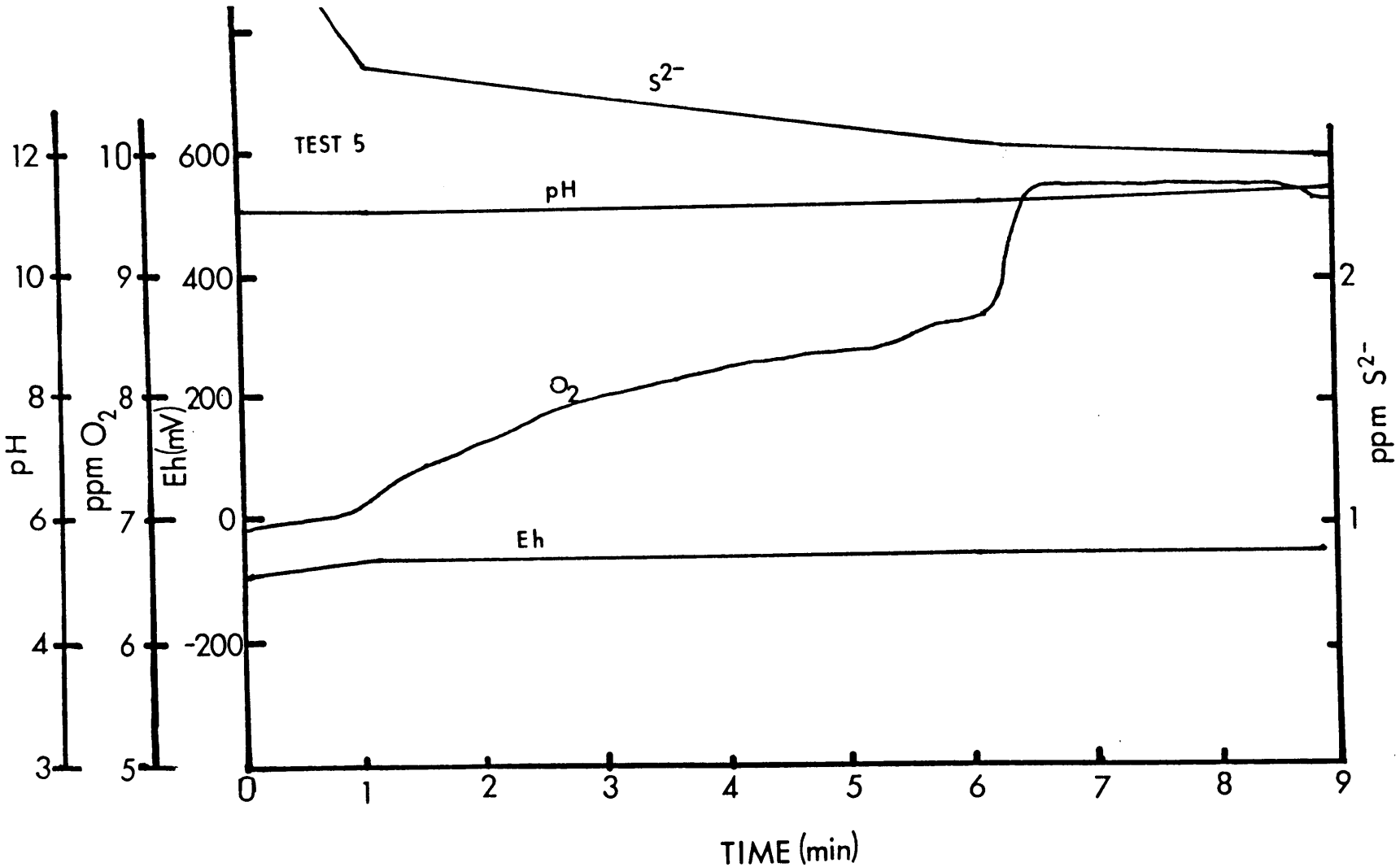
PK	ENERGY	MAX	FWHH	AREA
1G	168.60	13.50	1.70	8.8
2G	167.40	27.00	1.70	17.8
3G	167.50	35.00	1.70	23.0
4G	166.30	70.00	1.70	46.1

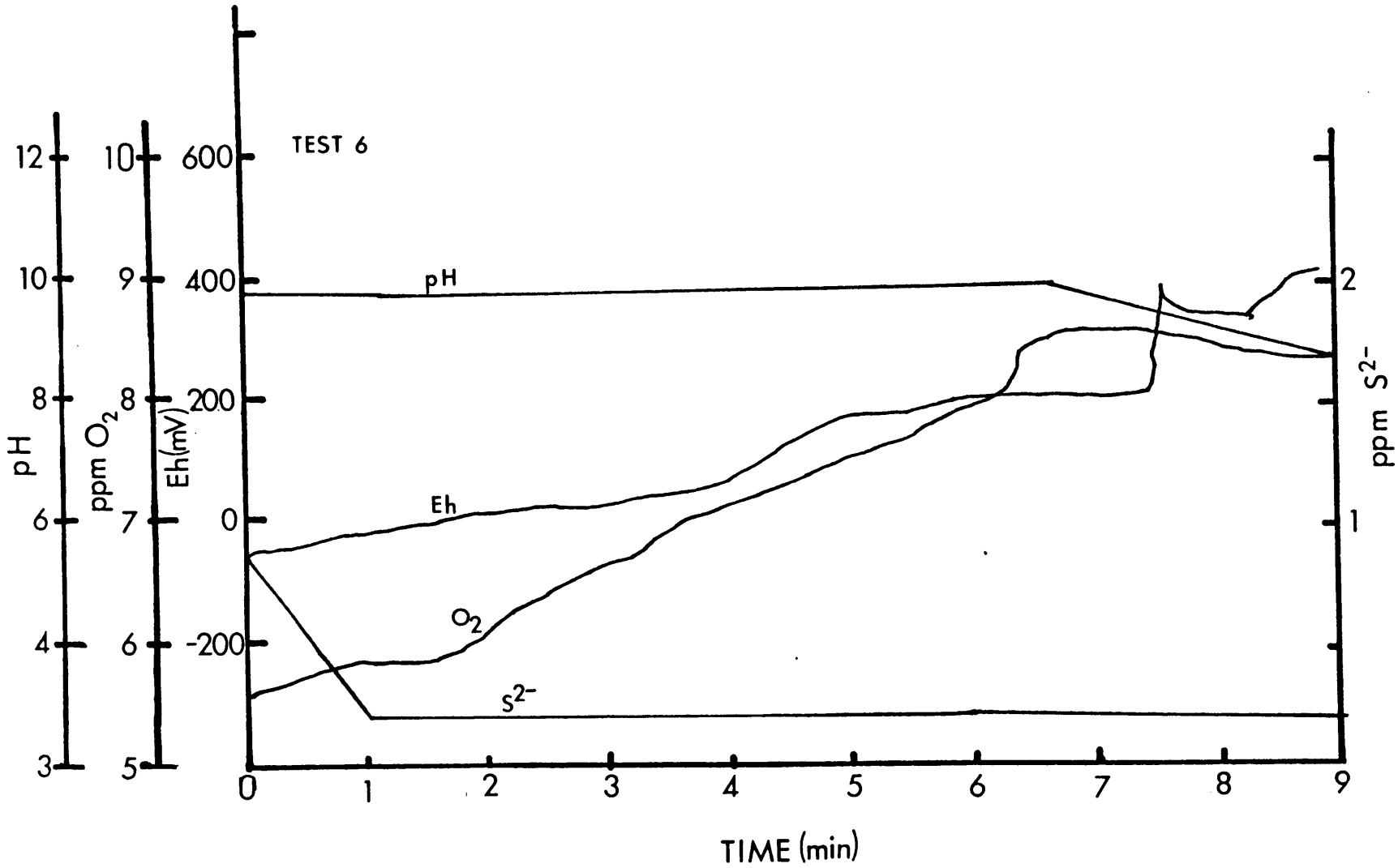


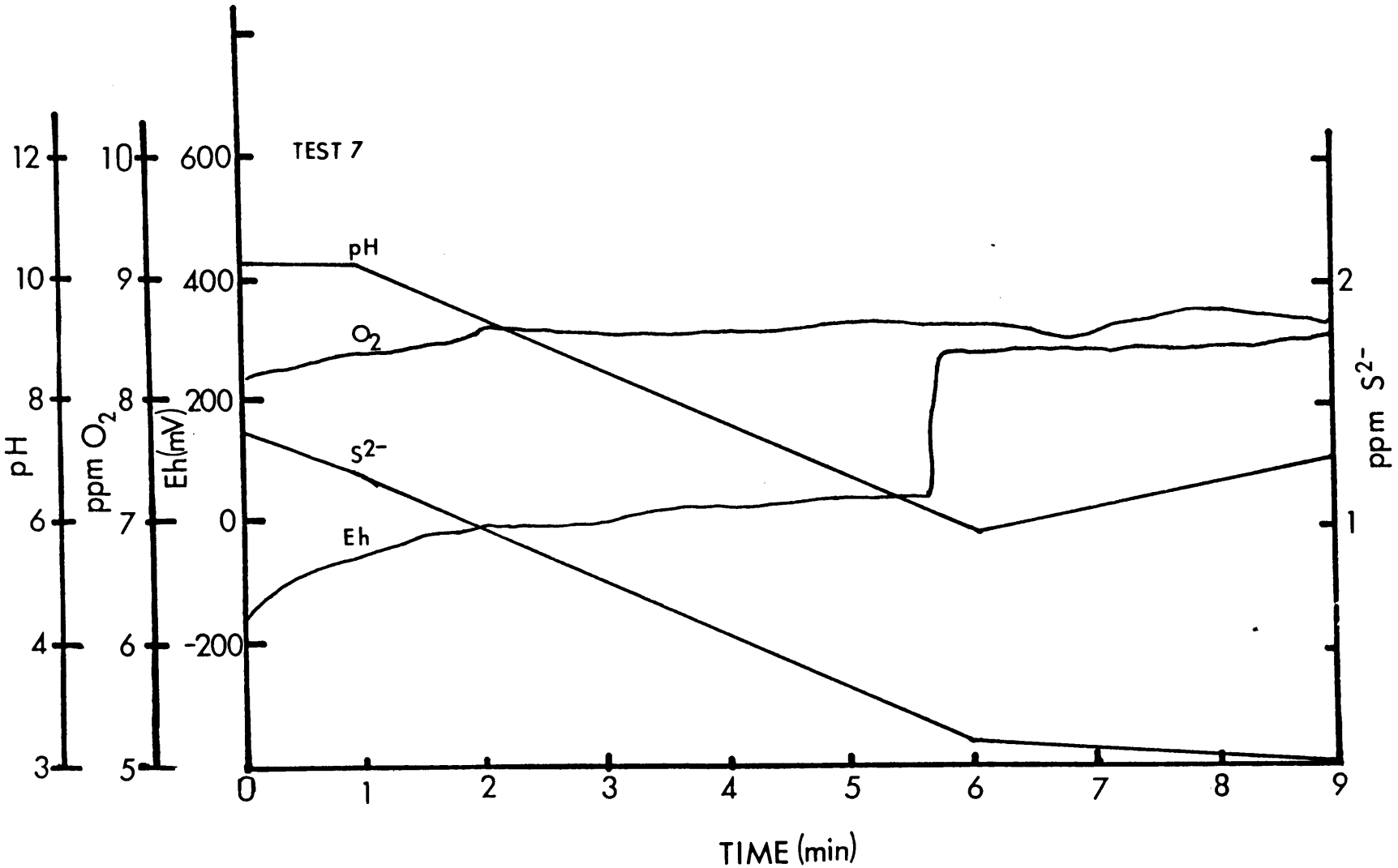
APPENDIX D: RECORDS OF OPERATING ELECTRODES IN BATCH FLOTATION

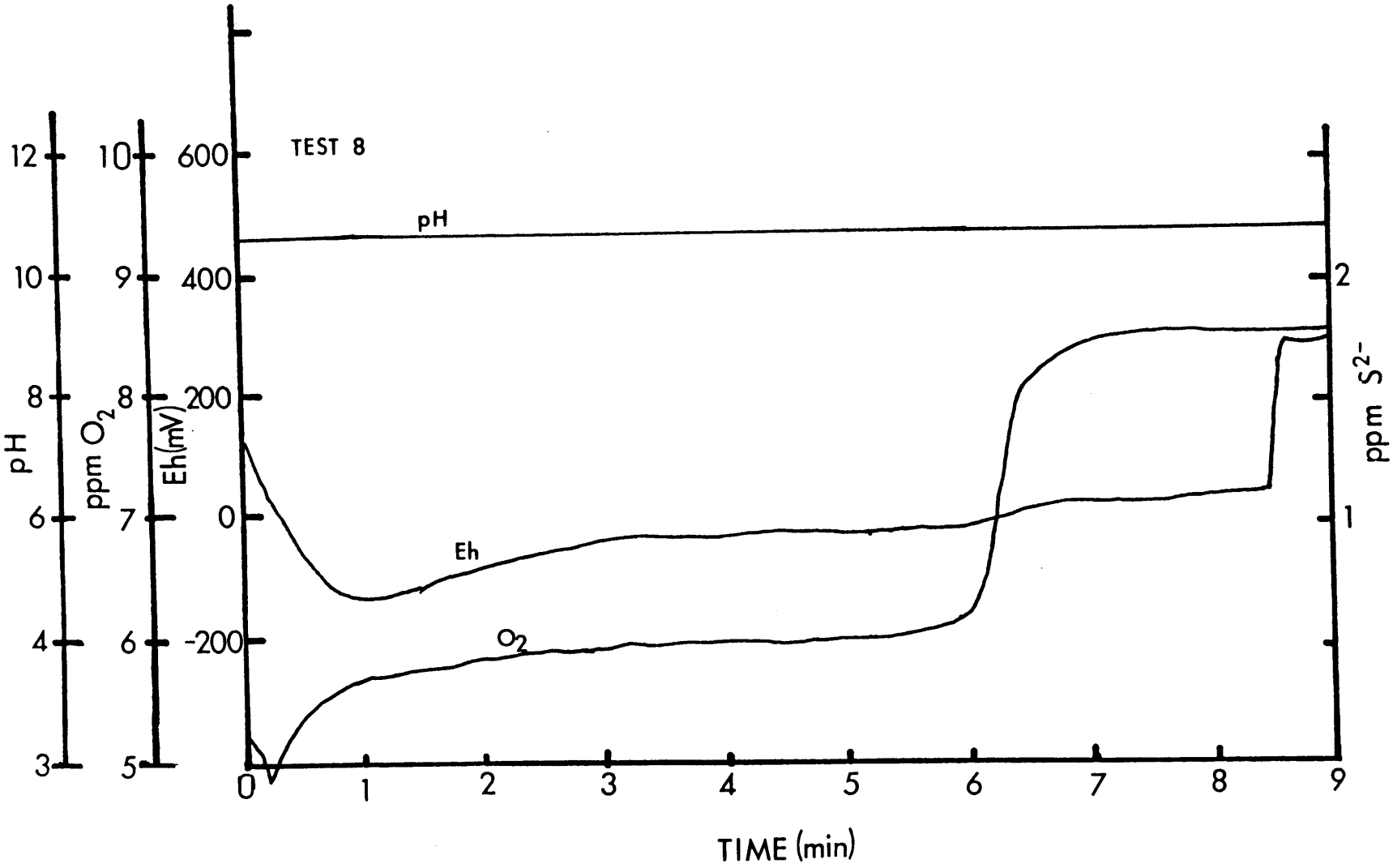

TEST 2
Eh
pH
O_2
O_2
pH
ppm O_2
Eh(mV)
ppm S^{2-}
TIME (min)
12
10
8
6
4
3
10
9
8
7
6
5
600
400
200
0
-200
2
1
0
1
2
3
4
5
6
7
8
9

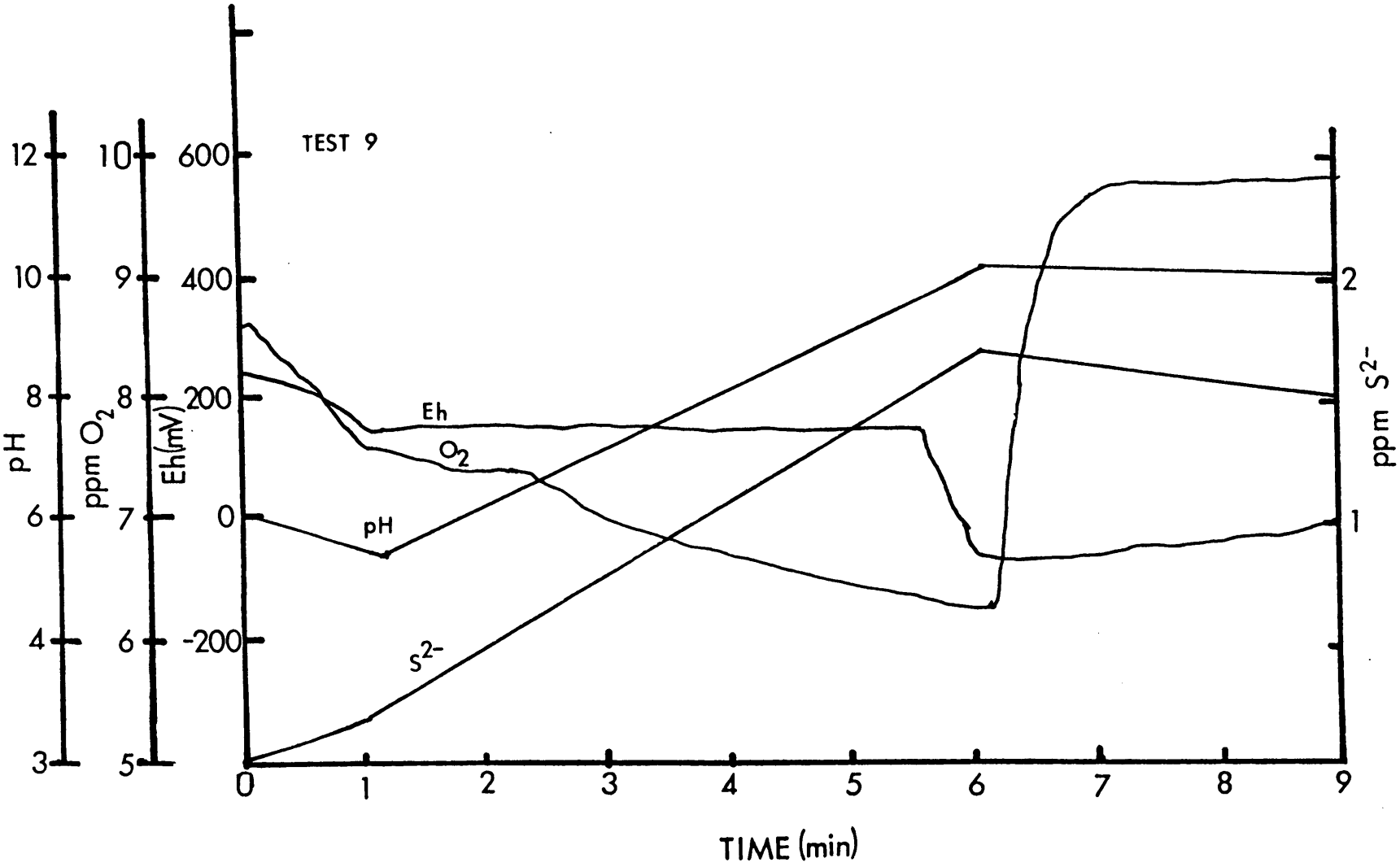

TEST 3
Eh
pH
O_2
pH
ppm O_2
Eh(mV)
ppm S^{2-}
TIME (min)
12
10
8
6
4
3
10
9
8
7
6
5
600
400
200
0
-200
2
1
0
1
2
3
4
5
6
7
8
9

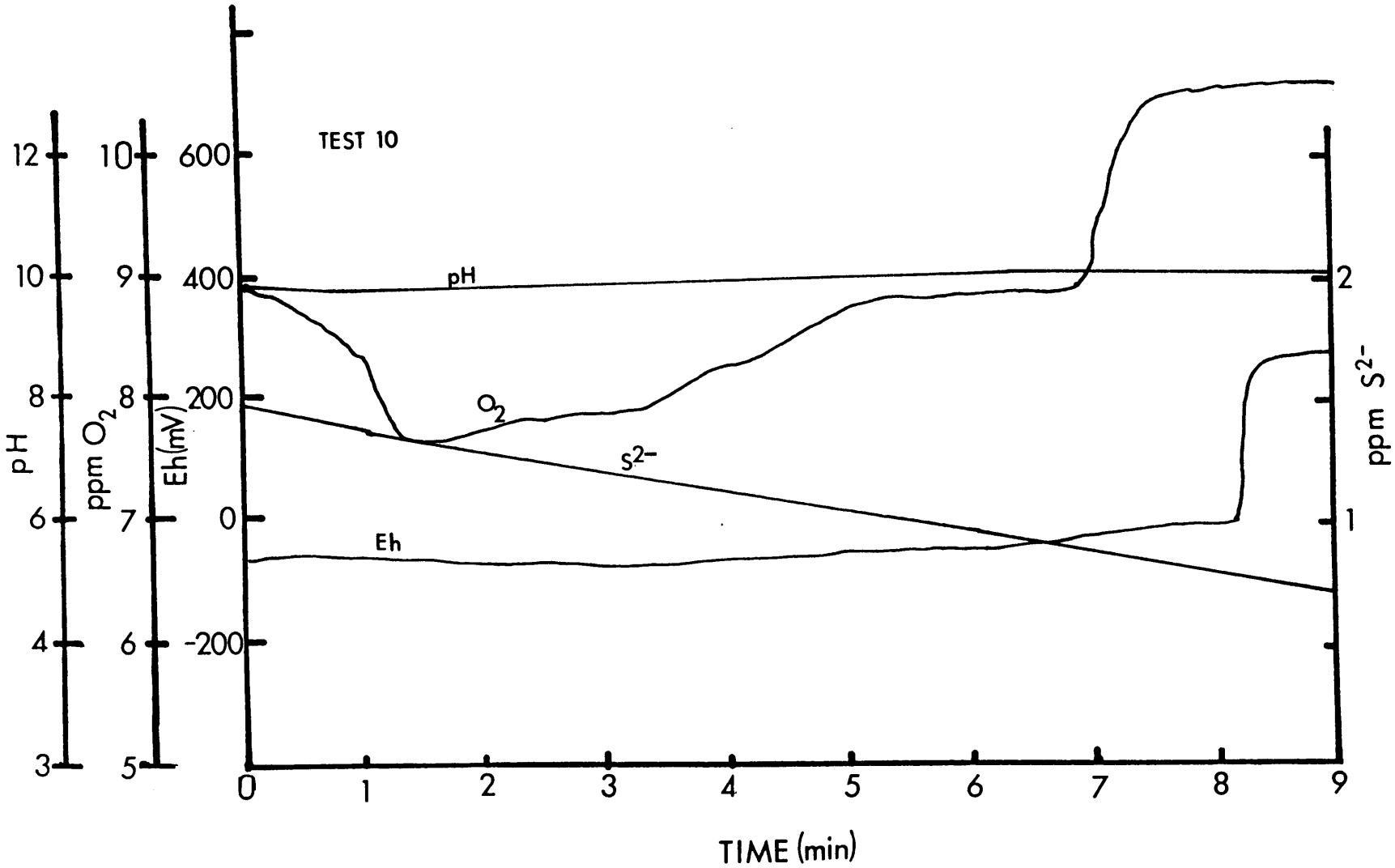

TEST 5
S^{2-}
pH
O_2
Eh
pH
ppm O_2
Eh(mV)
ppm S^{2-}
TIME (min)
12
10
8
6
4
3
10
9
8
7
6
5
600
400
200
0
-200
2
1
0
1
2
3
4
5
6
7
8
9

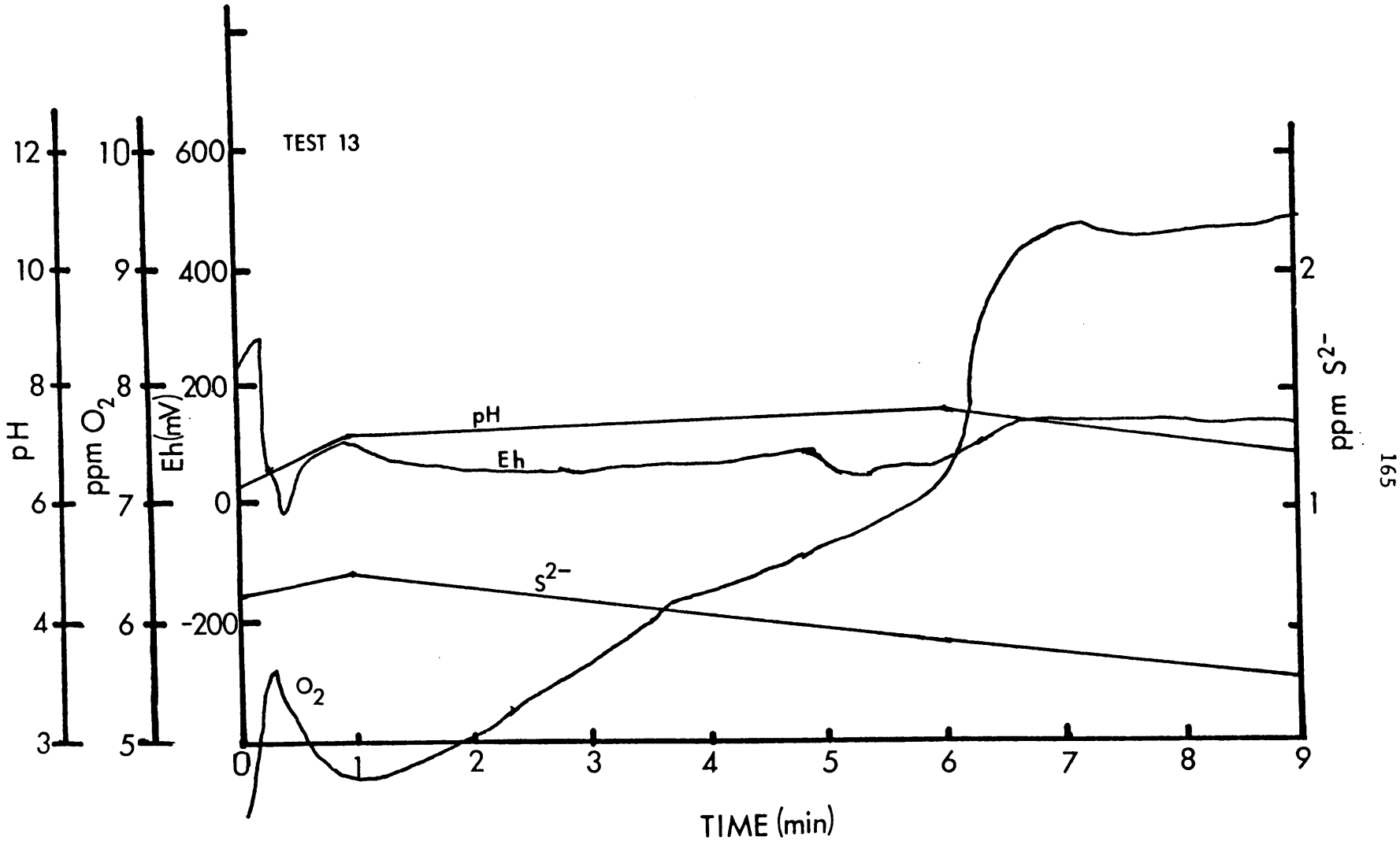

TEST 6
pH
ppm O_2
Eh(mV)
ppm S^{2-}
pH
Eh
O_2
S^{2-}
TIME (min)
12
10
8
6
4
3
10
9
8
7
6
5
600
400
200
0
-200
2
1
0
1
2
3
4
5
6
7
8
9

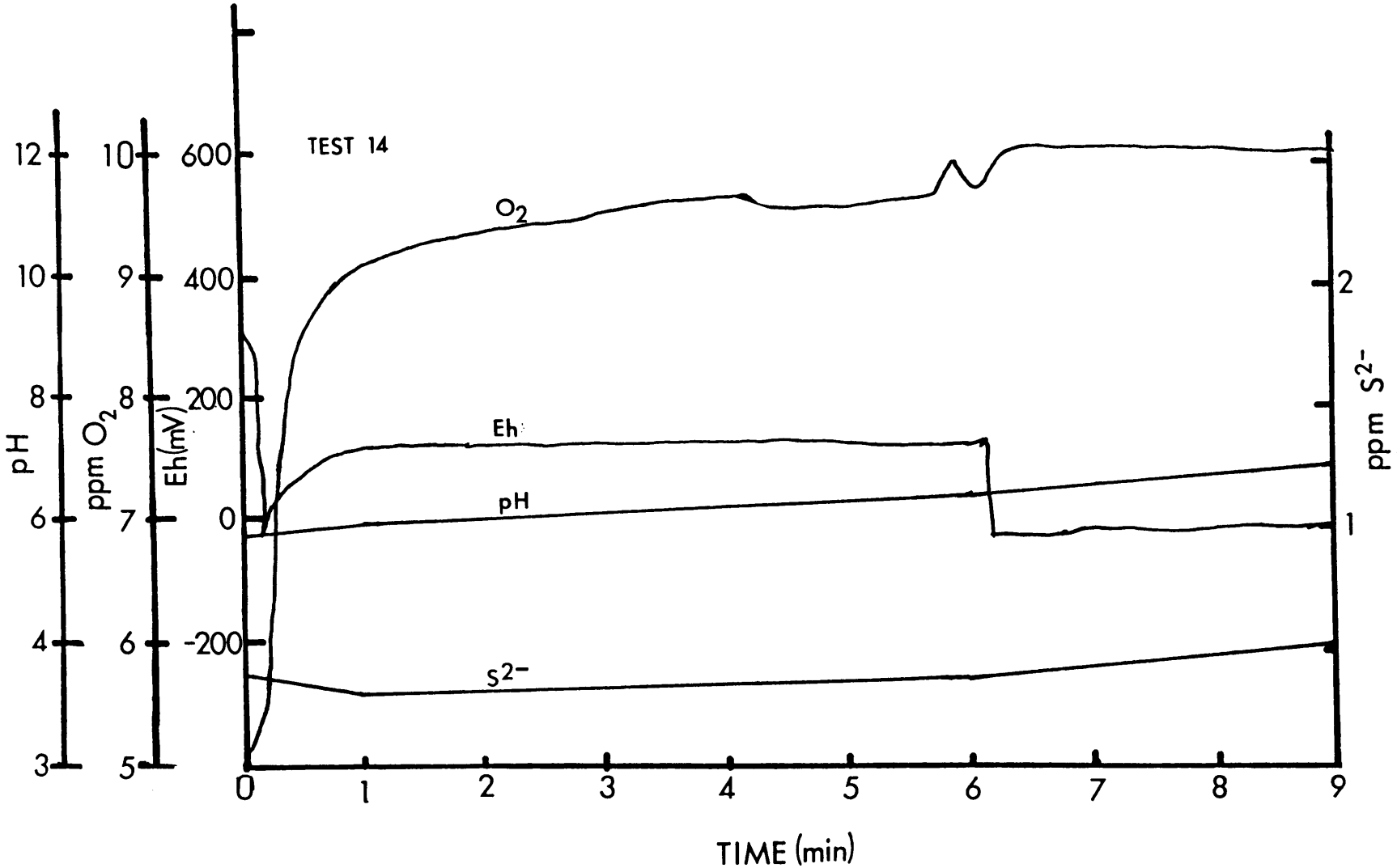

TEST 7
pH
O_2
S^{2-}
Eh
pH
ppm O_2
Eh(mV)
ppm S^{2-}
TIME (min)
12
10
8
6
4
3
10
9
8
7
6
5
600
400
200
0
-200
2
1
0
1
2
3
4
5
6
7
8
9

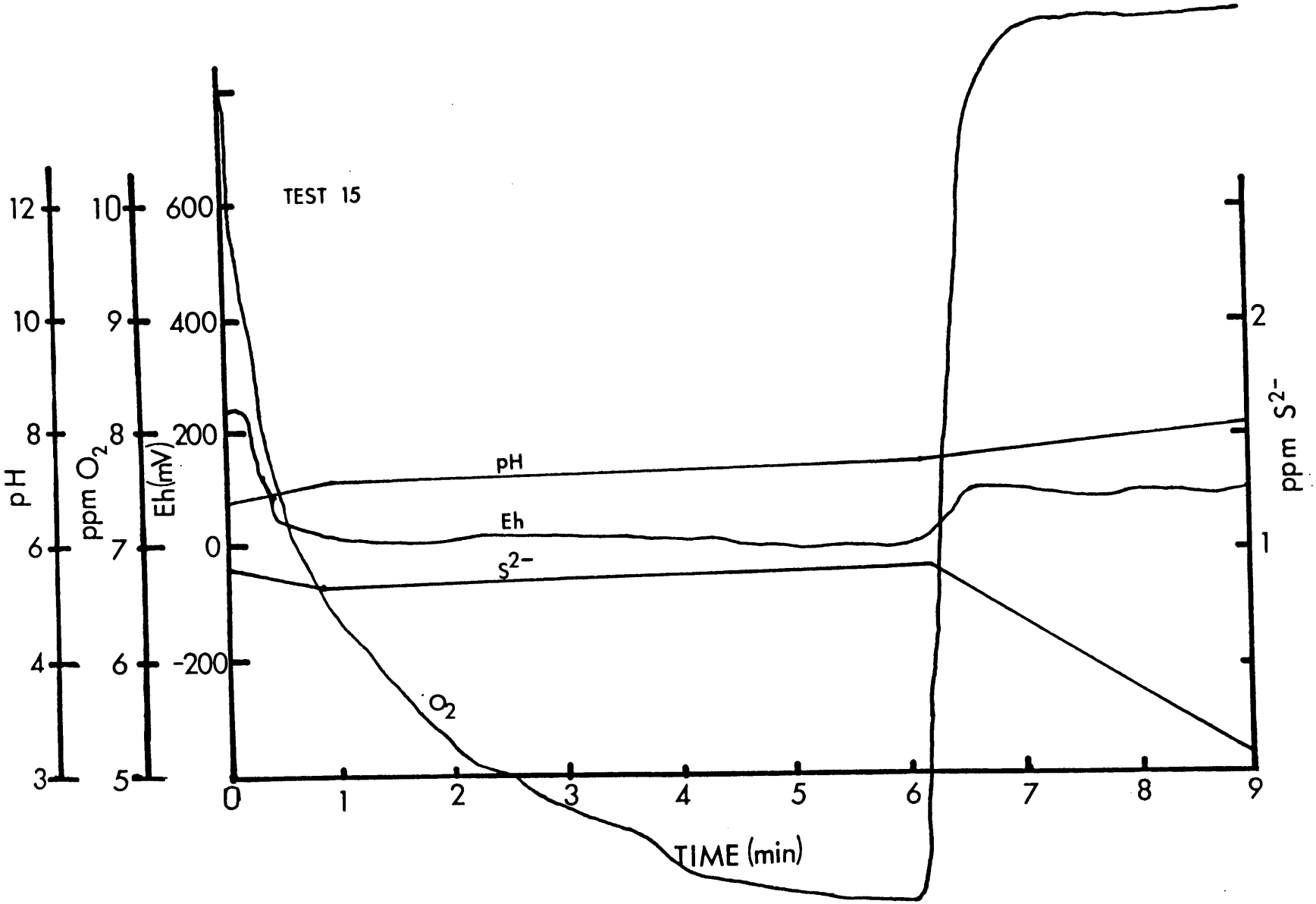

TEST 8
pH
Eh
O_2
pH
ppm O_2
Eh(mV)
ppm S^{2-}
TIME (min)
12
10
8
6
4
3
10
9
8
7
6
5
600
400
200
0
-200
2
1
0
1
2
3
4
5
6
7
8
9

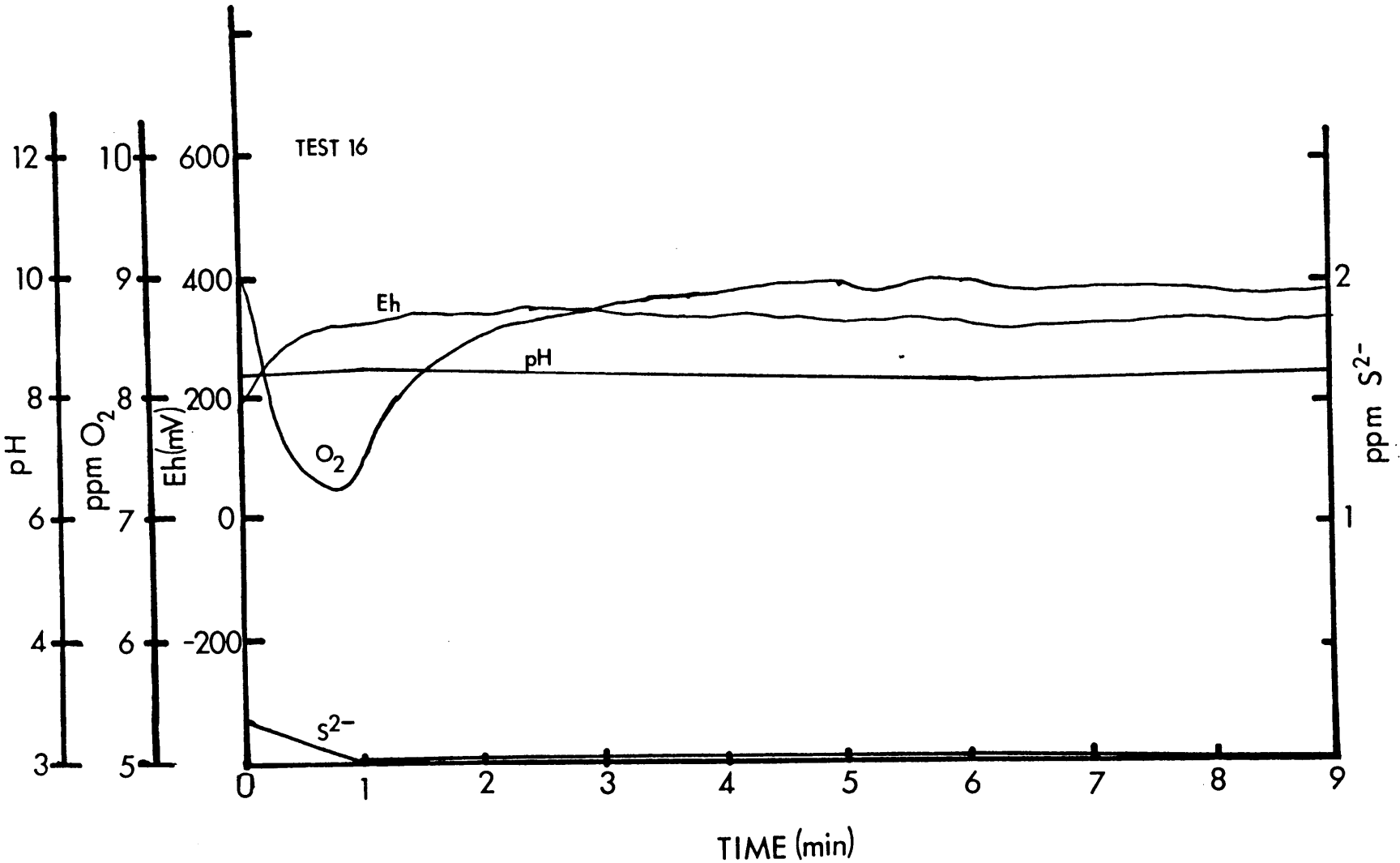

TEST 9
pH
ppm O_2
Eh(mV)
ppm S^{2-}
Eh
O_2
pH
S^{2-}
TIME (min)
12
10
8
6
4
3
10
9
8
7
6
5
600
400
200
0
-200
2
1
0
1
2
3
4
5
6
7
8
9

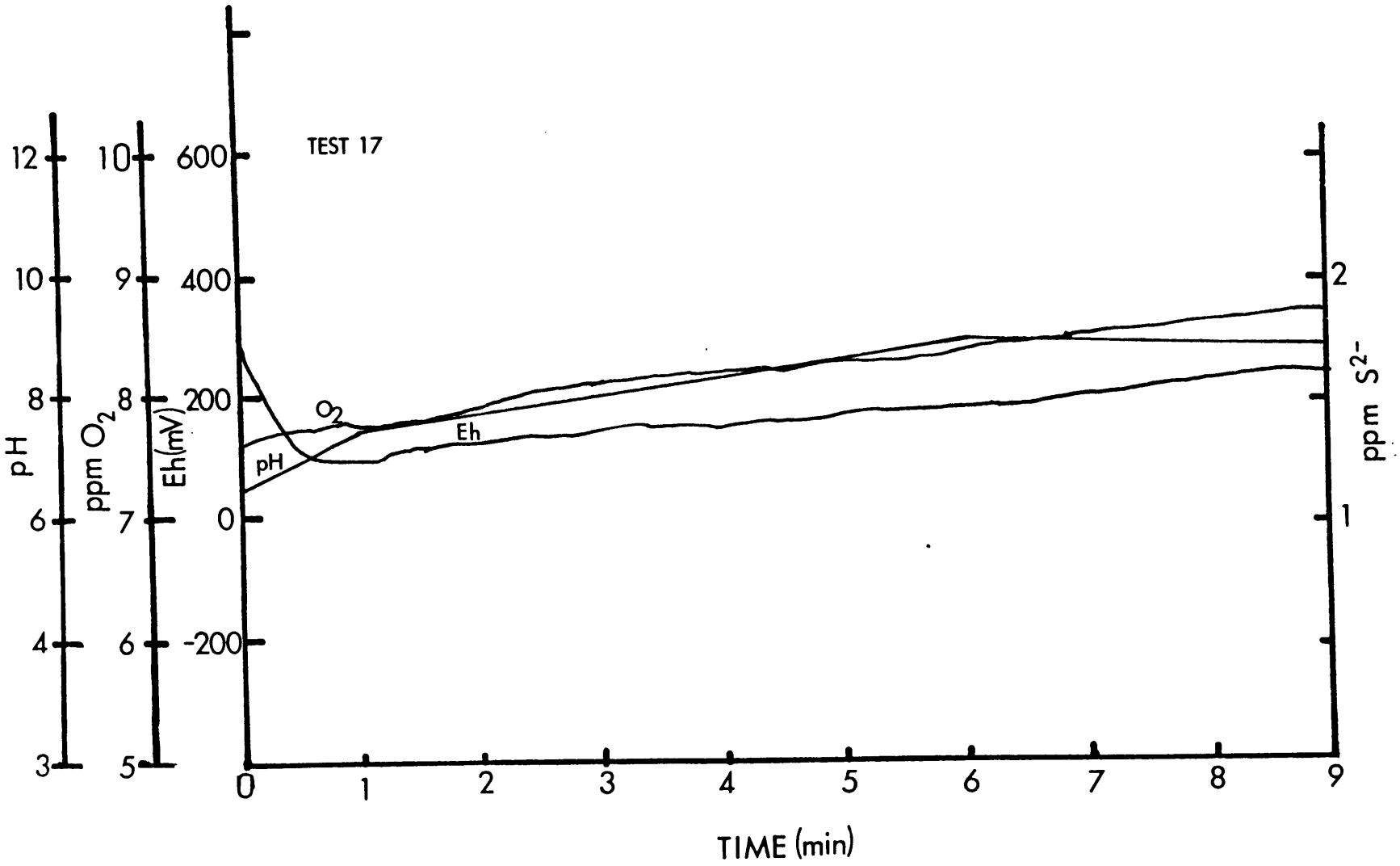

TEST 10
pH
ppm O_2
Eh(mV)
ppm S^{2-}
pH
O_2
S^{2-}
Eh
TIME (min)
12
10
8
6
4
3
10
9
8
7
6
5
600
400
200
0
-200
0
1
2
3
4
5
6
7
8
9
2
1

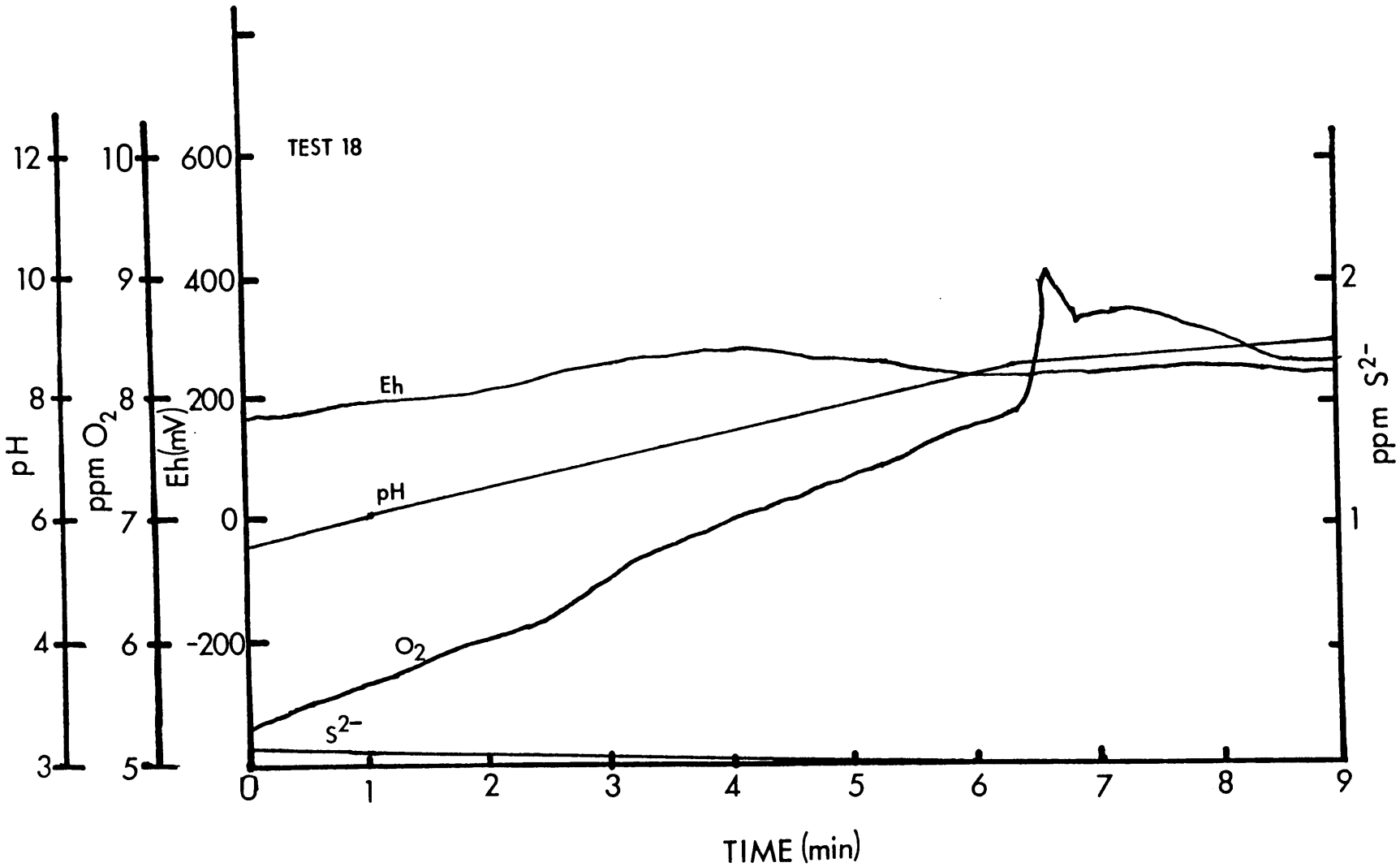

TEST 13
pH
ppm O_2
Eh(mV)
ppm S^{2-}
pH
Eh
S^{2-}
O_2
TIME (min)
12
10
8
6
4
3
10
9
8
7
6
5
600
400
200
0
-200
2
1
0
1
2
3
4
5
6
7
8
9

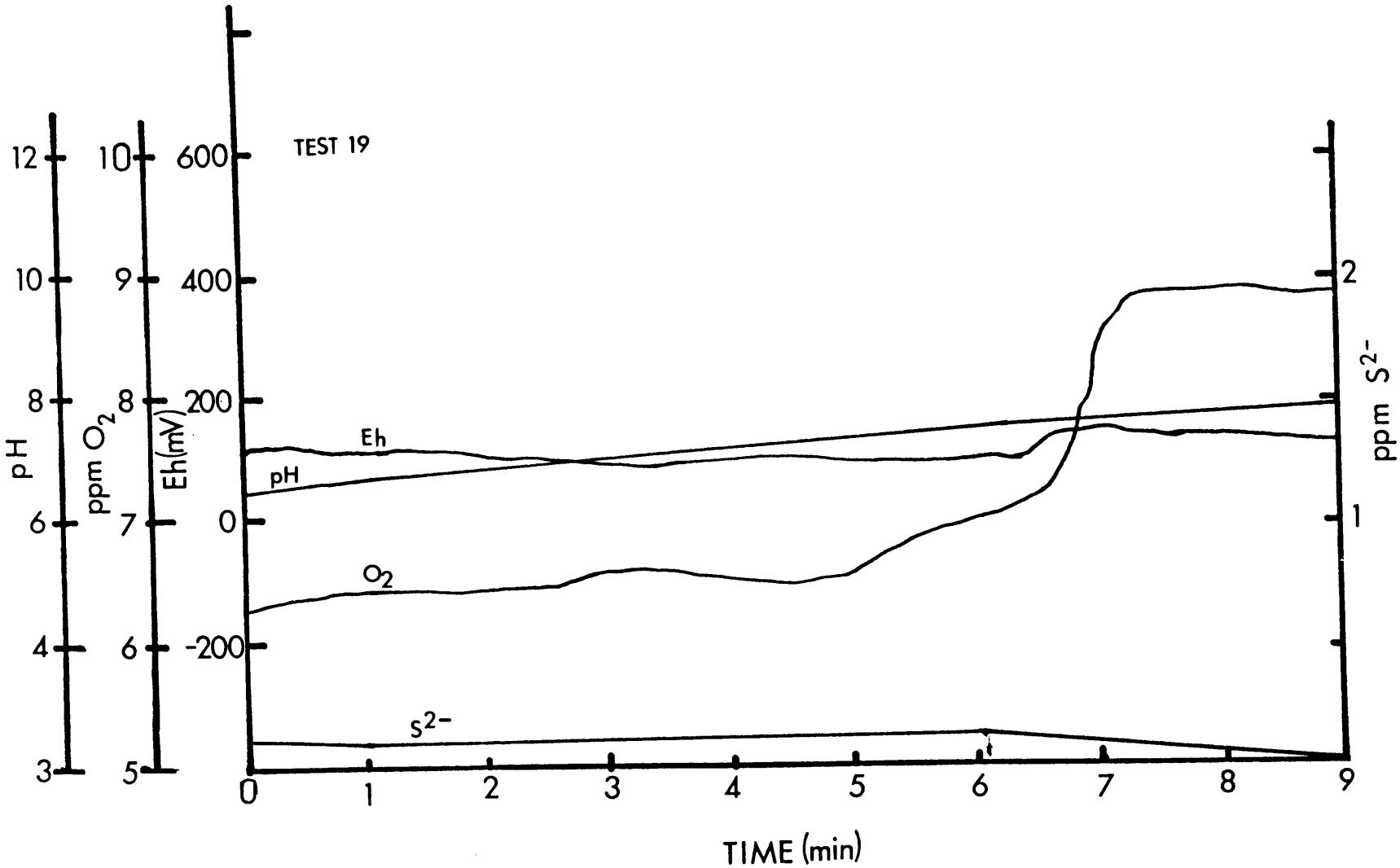

TEST 14
pH
ppm O_2
Eh(mV)
ppm S^{2-}
O_2
Eh
pH
S^{2-}
TIME (min)
12
10
8
6
4
3
10
9
8
7
6
5
600
400
200
0
-200
2
1
0
1
2
3
4
5
6
7
8
9

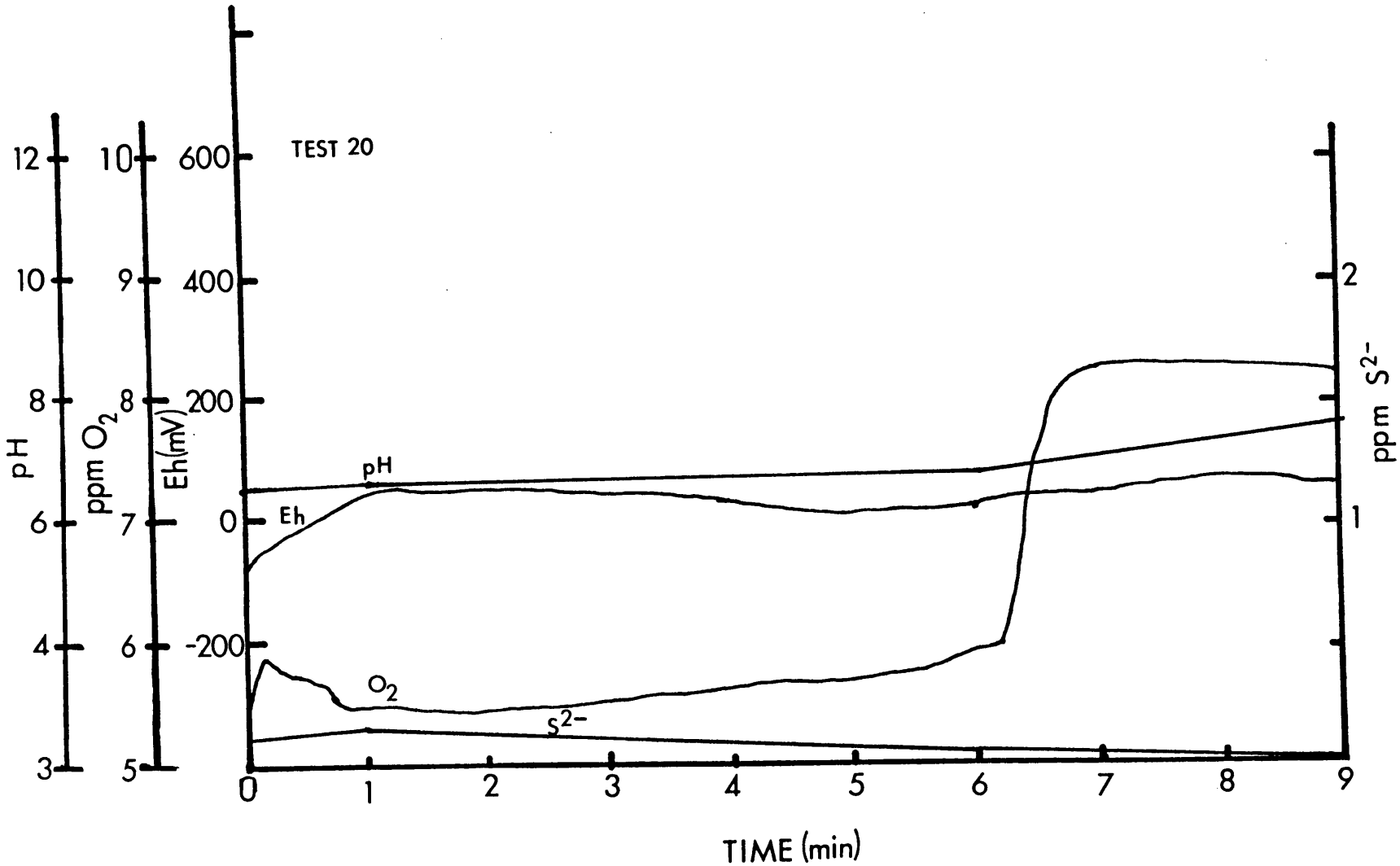

TEST 15
pH
ppm O_2
Eh(mV)
ppm S^{2-}
pH
Eh
S^{2-}
O_2
TIME (min)
12
10
8
6
4
3
10
9
8
7
6
5
600
400
200
0
-200
2
1
0
1
2
3
4
5
6
7
8
9

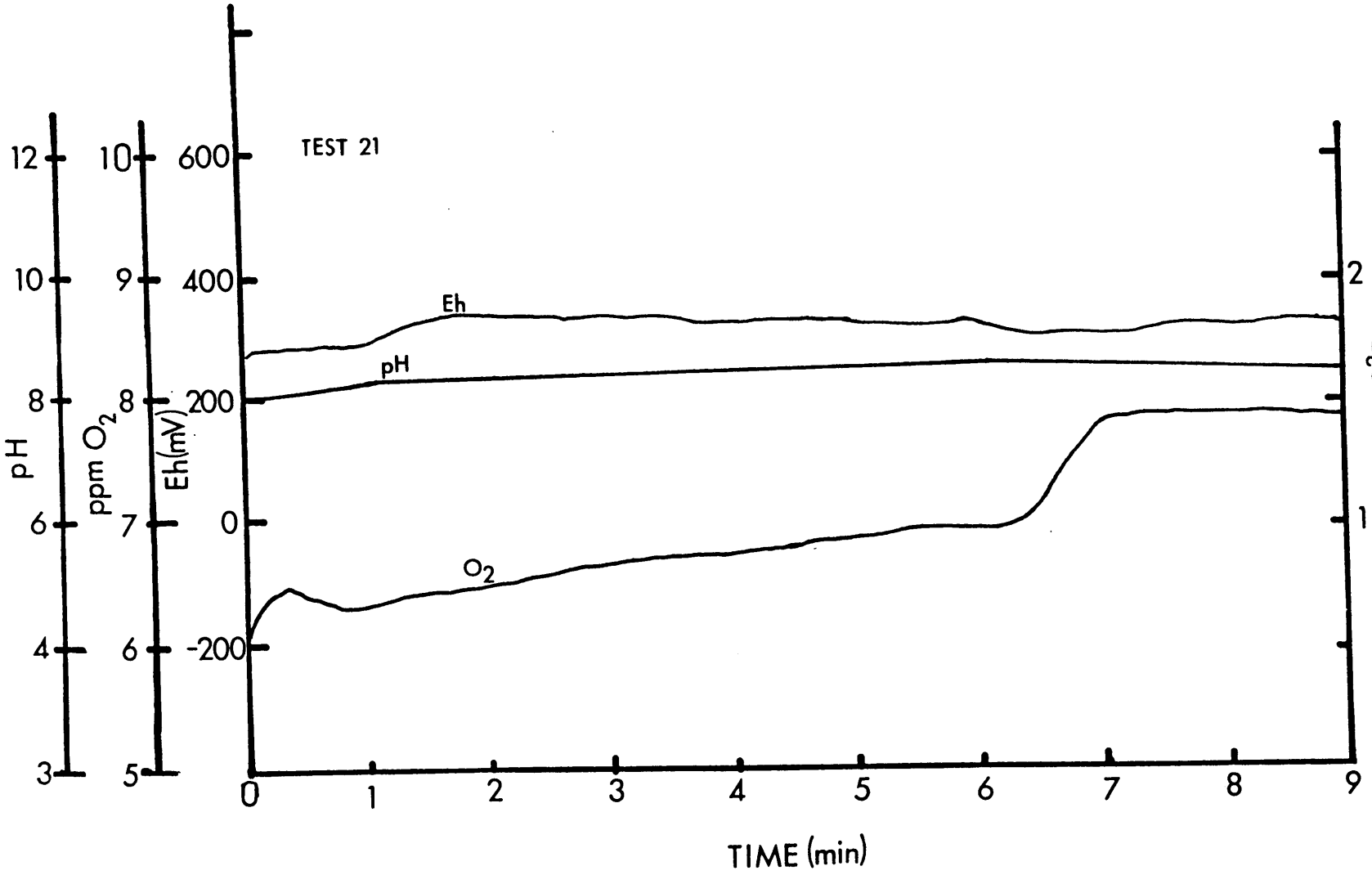

TEST 16
pH
ppm O_2
Eh(mV)
ppm S^{2-}
Eh
pH
O_2
S^{2-}
TIME (min)
12
10
8
6
4
3
10
9
8
7
6
5
600
400
200
0
-200
2
1
0
1
2
3
4
5
6
7
8
9

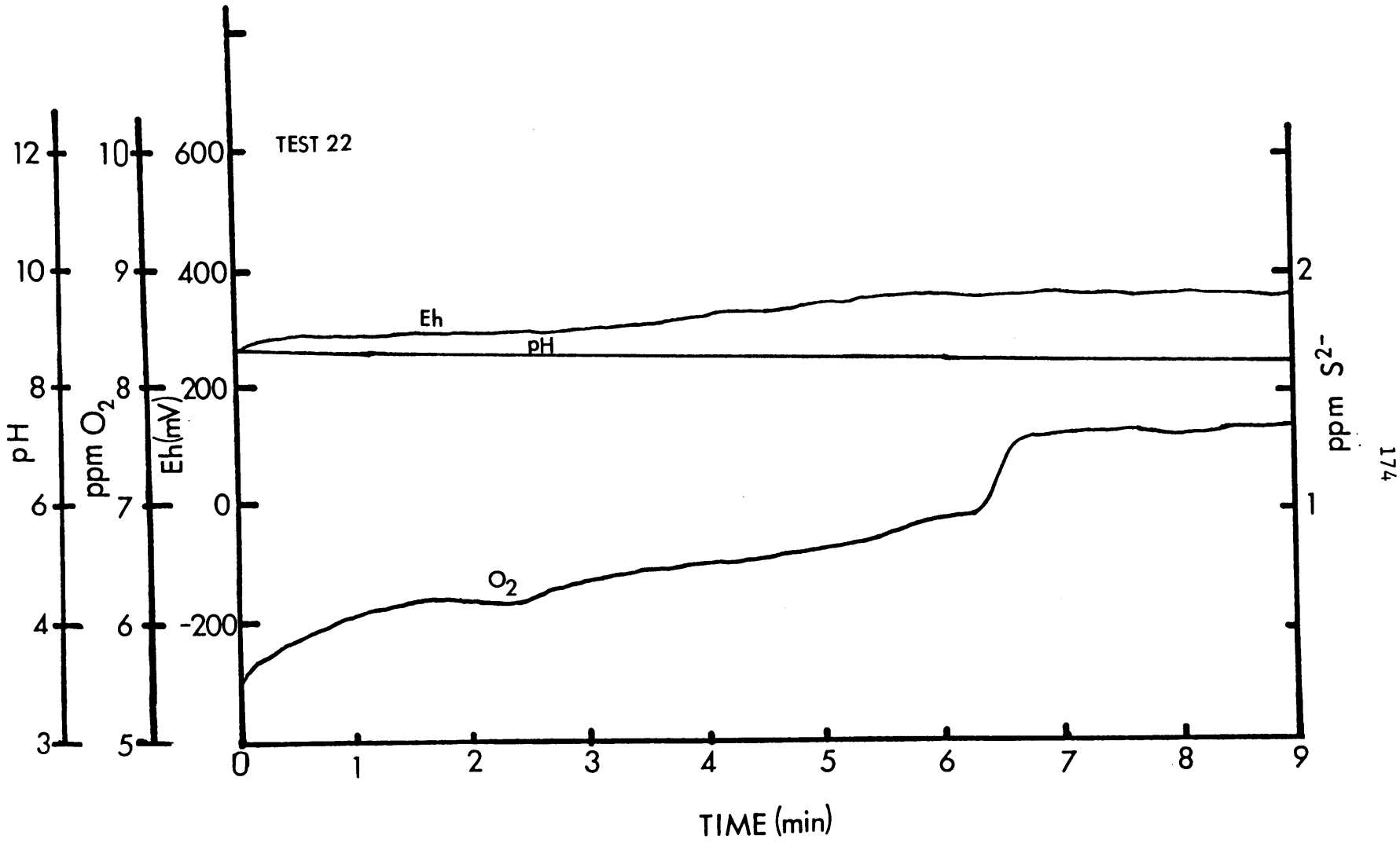

TEST 17
pH
ppm O_2
Eh(mV)
ppm S^{2-}
O_2
Eh
pH
TIME (min)
12
10
8
6
4
3
10
9
8
7
6
5
600
400
200
0
-200
2
1
0
1
2
3
4
5
6
7
8
9

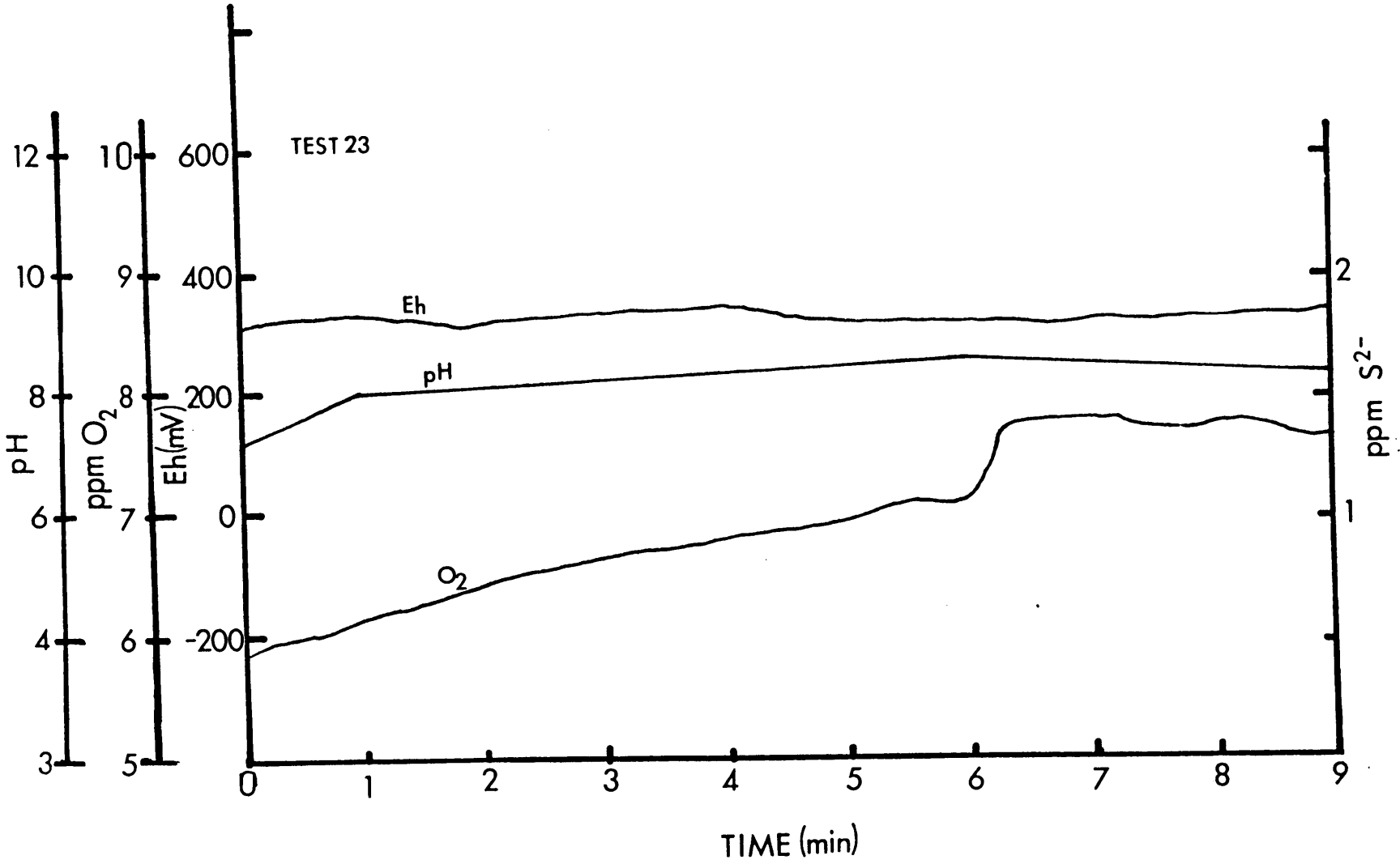

TEST 18
pH
ppm O_2
Eh(mV)
ppm S^{2-}
Eh
pH
O_2
S^{2-}
TIME (min)
12
10
8
6
4
3
10
9
8
7
6
5
600
400
200
0
-200
2
1
0
1
2
3
4
5
6
7
8
9

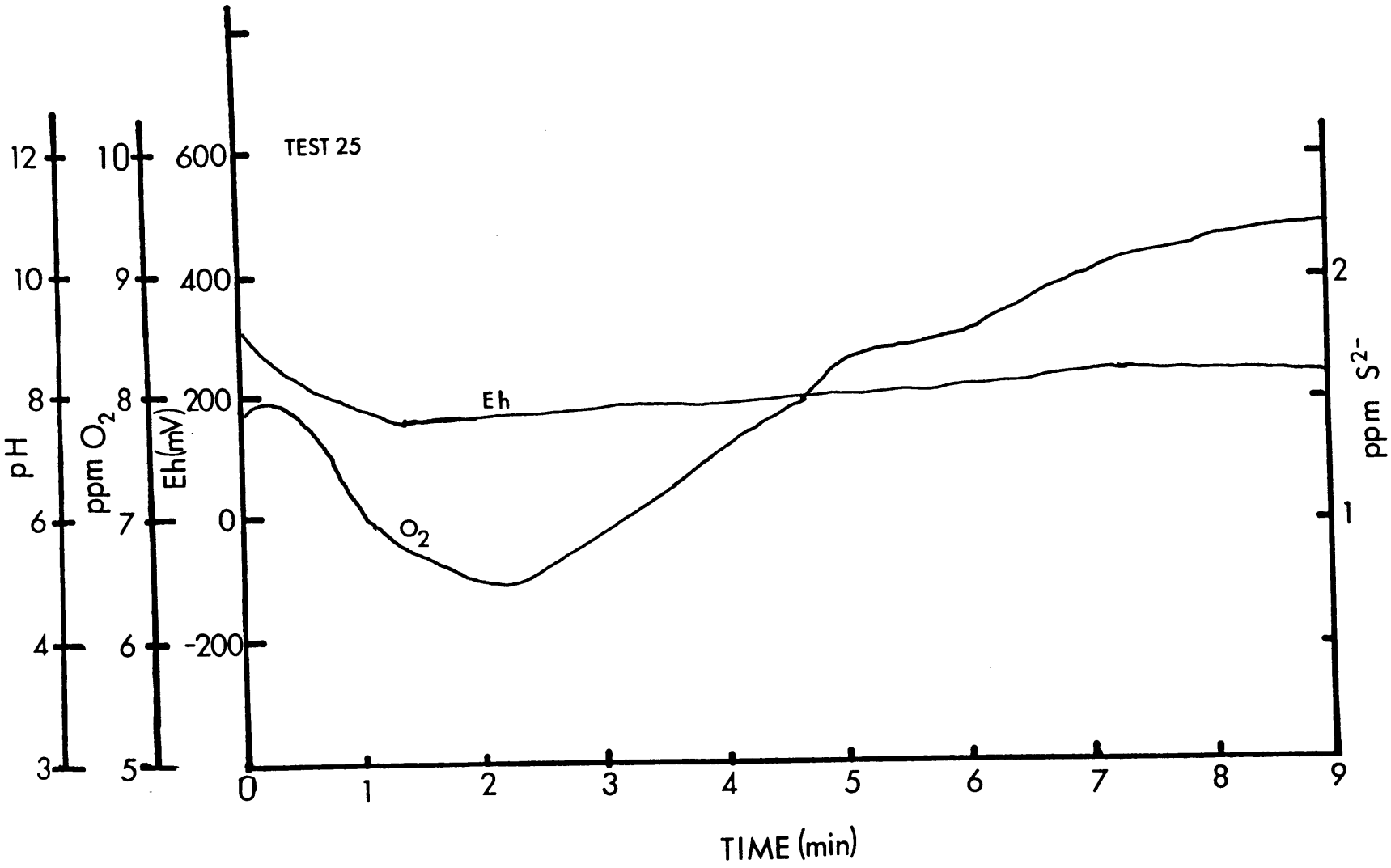

TEST 19
pH
ppm O_2
Eh(mV)
ppm S^{2-}
Eh
pH
O_2
S^{2-}
TIME (min)
12
10
8
6
4
3
10
9
8
7
6
5
600
400
200
0
-200
2
1
0
1
2
3
4
5
6
7
8
9

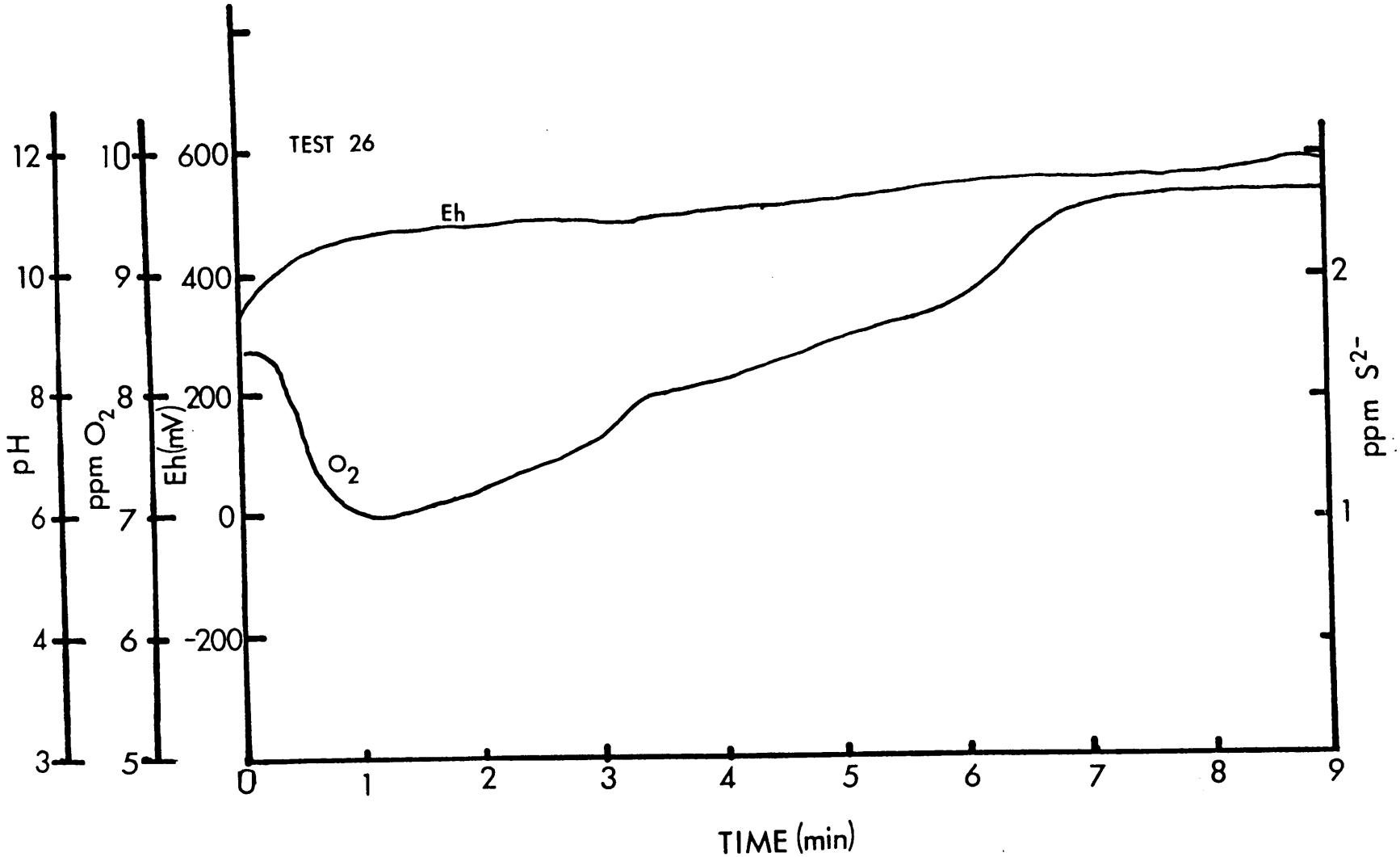

TEST 20
pH
ppm O_2
Eh(mV)
ppm S^{2-}
pH
Eh
O_2
S^{2-}
TIME (min)
12
10
8
6
4
3
10
9
8
7
6
5
600
400
200
0
-200
2
1
0
1
2
3
4
5
6
7
8
9

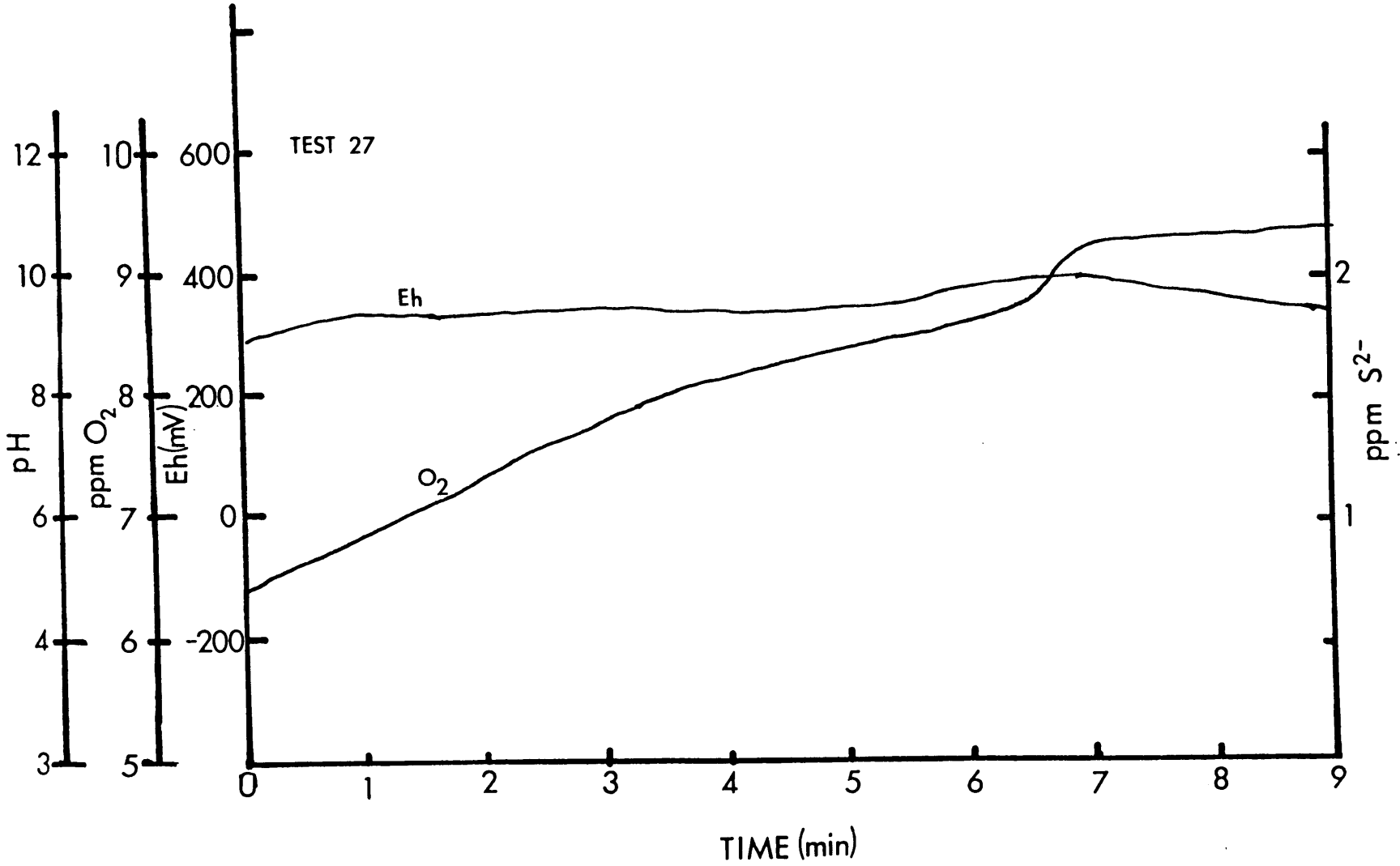

TEST 21
pH
ppm O_2
Eh(mV)
ppm S^{2-}
Eh
pH
O_2
TIME (min)
12
10
8
6
4
3
10
9
8
7
6
5
600
400
200
0
-200
2
1
0
1
2
3
4
5
6
7
8
9

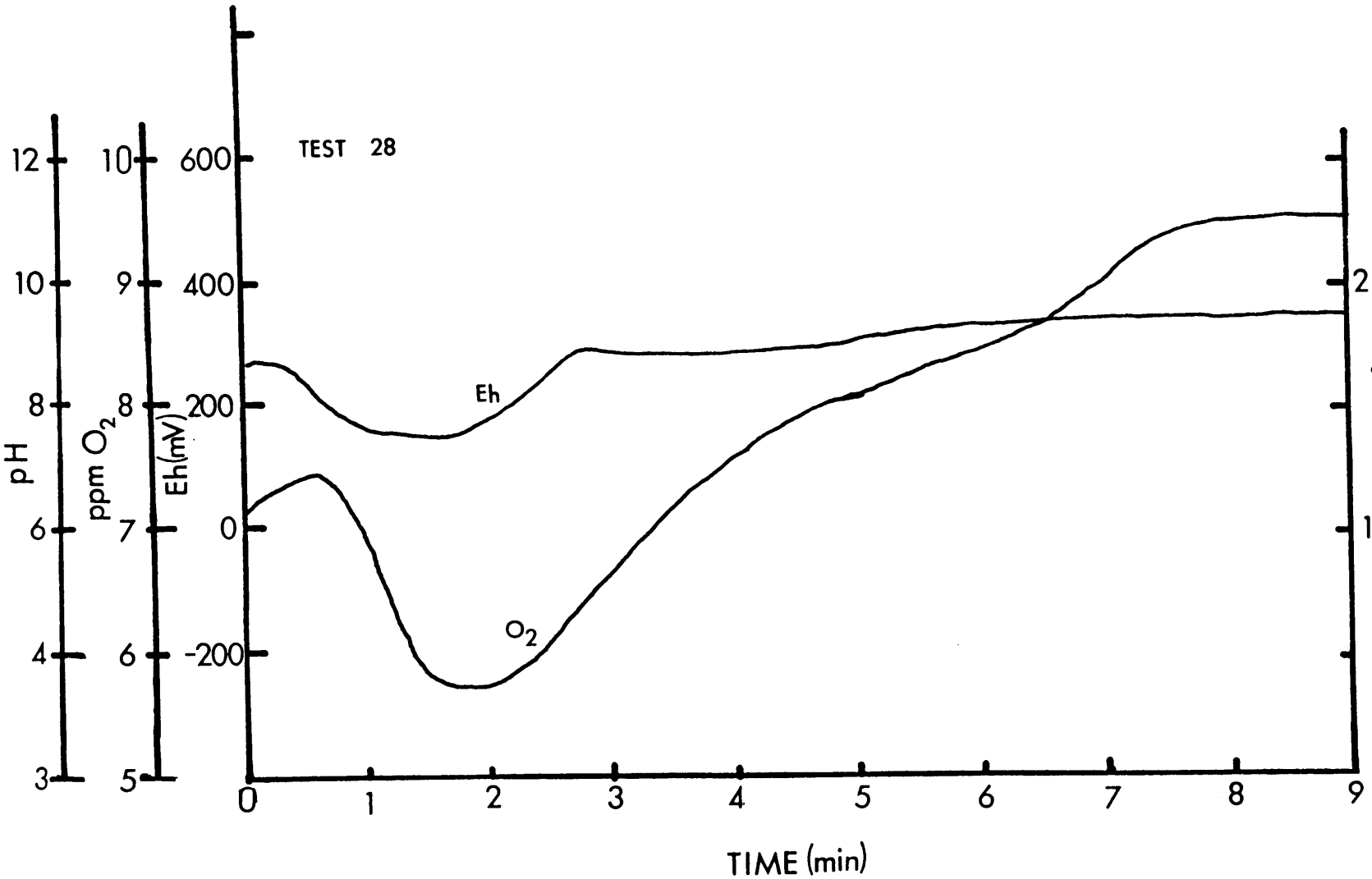

TEST 22
pH
ppm O_2
Eh(mV)
ppm S^{2-}
Eh
pH
O_2
TIME (min)
12
10
8
6
4
3
10
9
8
7
6
5
600
400
200
0
-200
2
1
0
1
2
3
4
5
6
7
8
9

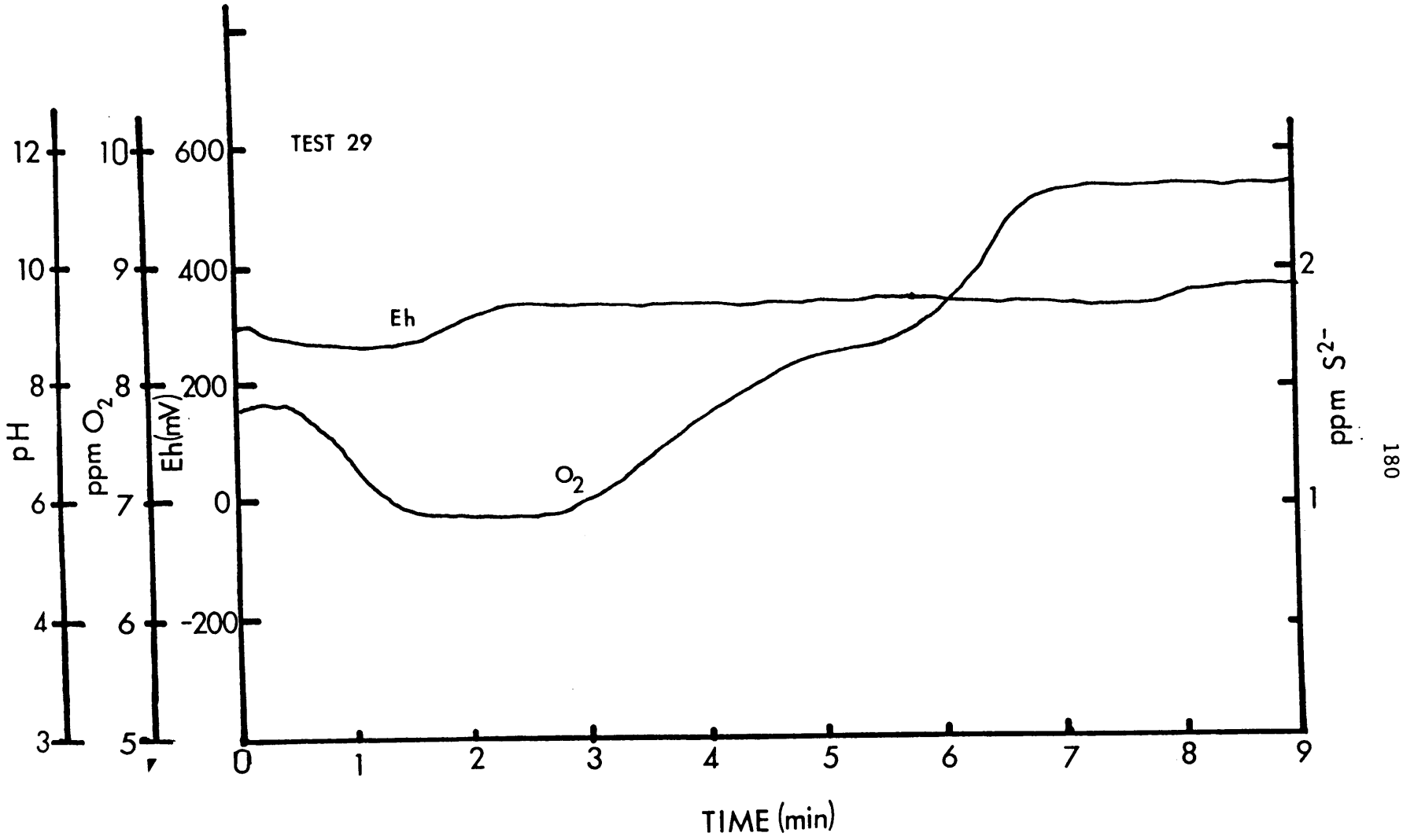

TEST 23
Eh
pH
O_2
pH
ppm O_2
Eh(mV)
ppm S^{2-}
TIME (min)
12
10
8
6
4
3
10
9
8
7
6
5
600
400
200
0
-200
2
1
0
1
2
3
4
5
6
7
8
9


TEST 25
pH
ppm O_2
Eh(mV)
ppm S^{2-}
Eh
O_2
TIME (min)
12
10
8
6
4
3
10
9
8
7
6
5
600
400
200
0
-200
2
1
0
1
2
3
4
5
6
7
8
9

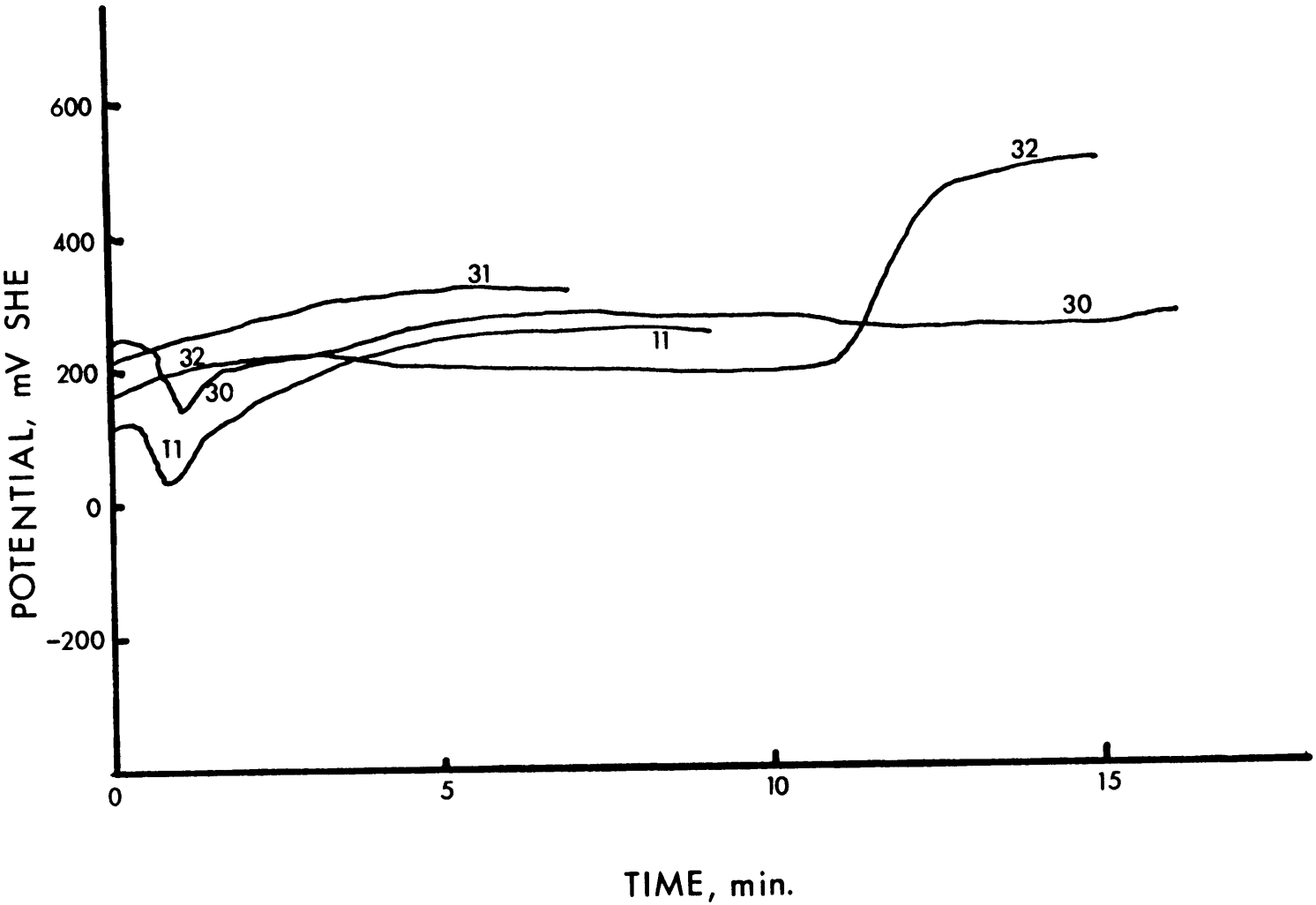

TEST 26
Eh
O_2
pH
ppm O_2
Eh(mV)
ppm S^{2-}
TIME (min)
12
10
8
6
4
3
10
9
8
7
6
5
600
400
200
0
-200
2
1
0
1
2
3
4
5
6
7
8
9

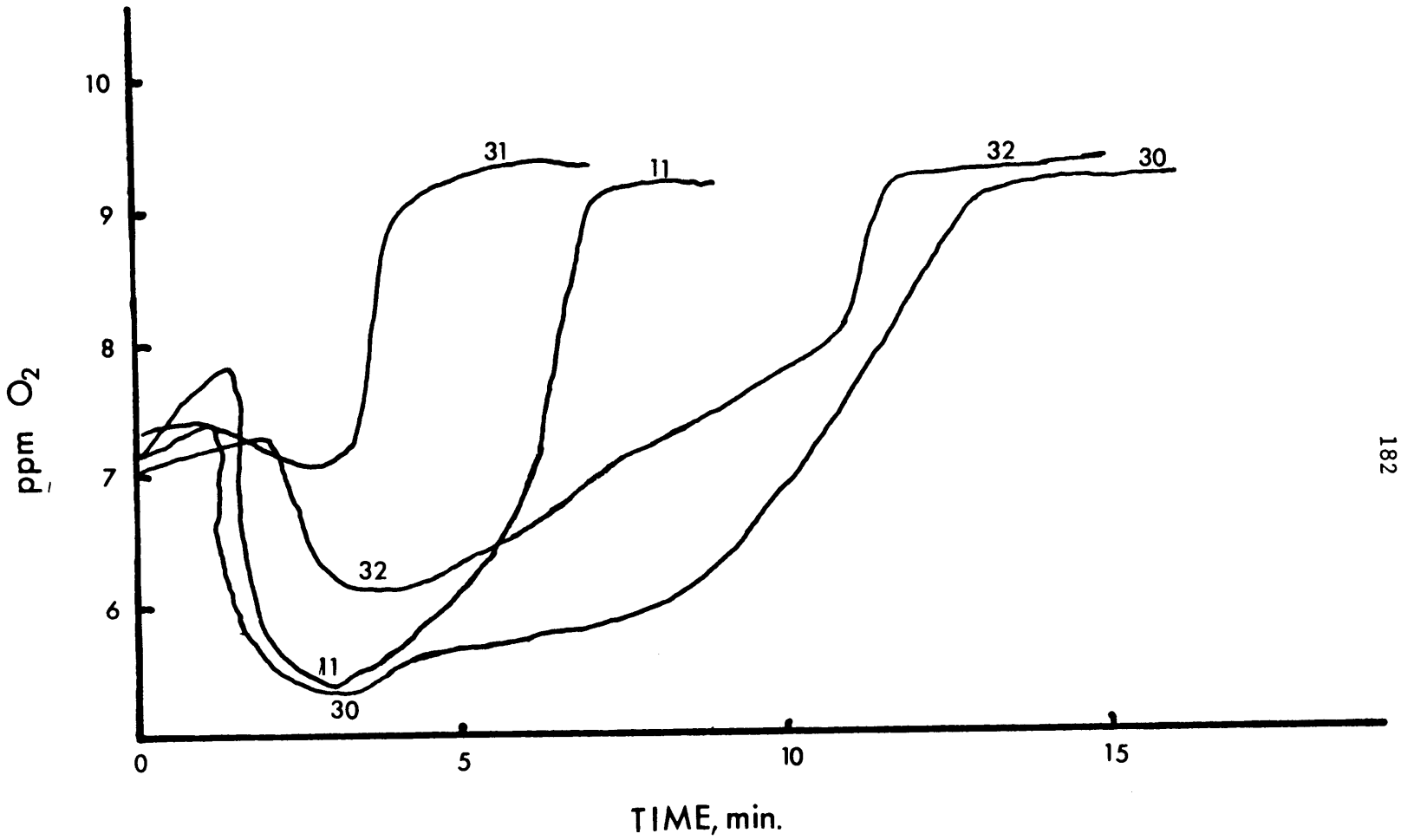

TEST 27
Eh
O_2
pH
ppm O_2
Eh(mV)
ppm S^{2-}
TIME (min)
12
10
8
6
4
3
10
9
8
7
6
5
600
400
200
0
-200
2
1
0
1
2
3
4
5
6
7
8
9


TEST 28
pH
ppm O_2
Eh(mV)
ppm S^{2-}
Eh
O_2
TIME (min)
12
10
8
6
4
3
10
9
8
7
6
5
600
400
200
0
-200
2
1
0
1
2
3
4
5
6
7
8
9


TEST 29
pH
ppm O_2
Eh(mV)
ppm S^{2-}
Eh
O_2
TIME (min)
12
10
8
6
4
3
10
9
8
7
6
5
600
400
200
0
-200
2
1
0
1
2
3
4
5
6
7
8
9

180


POTENTIAL, mV SHE
600
400
200
0
-200
0
5
10
15
TIME, min.
32
31
30
11
32
30
11


10
9
8
7
6
ppm O_2
31
11
32
30
32
11
30
0
5
10
15
TIME, min.

APPENDIX E: ASSAY PROCEDURE

ASSAY PROCEDURE

An amount of flotation product, between one-half and two grams, depending on the expected concentration, was accurately weighed into a 125-ml Erlenmeyer flask. Twenty ml of aqua regia (50% HCl-50% HNO_3) was added and the flask placed on a hotplate and heated to boiling. A reflux boiling funnel was placed in the mouth of the flask to prevent excessive splashing of the solution and to wash the sides of the flask. The sample was slowly boiled until the solution had nearly all evaporated. The sides of the flask were then rinsed with enough water to dissolve any metal ions.

The samples, thus digested, were allowed to cool and filtered through Whatman number 2 filter paper to remove any undissolved solids. The filtrate was then transferred to a volumetric flask and diluted with doubly distilled water. Further dilution was often necessary to bring the zinc concentration in the unknown sample to within the range of the calibration standards.

The zinc content of each sample was then determined using a Spectraspan IV Plasma Emission Spectro-

meter, set to detect zinc in the wavelength region around 2025.51 Angstroms. All glassware used in these procedures was cleaned in Micro cleaning solution, rinsed with tap water, soaked for a minimum of 2 hours in 20% HNO_3, then rinsed with distilled and doubly distilled water. This procedure was carried out to ensure that no extraneous metal ions would interfere with the analysis.

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