



Instrument development for piezoelectric detection of the aqueous cyanide ion
by Cassandra Joy Graber

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in
Chemistry

Montana State University

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Abstract:

Cyanide is present in many industrial effluents; however, standard methods of detection are often inadequate for regulating effluent waters. Piezoelectric cyanide detection as described in this paper presents an attractive alternative to the standard methods for cyanide determination due to its high sensitivity, simplicity, and lack of interference. A system was designed and built for cyanide detection. Electronic noise is eliminated by mixing two high frequency sine waves to produce a low frequency sine wave as input into a frequency counter. A reference crystal in the same environment as the sampling crystal is used to correct for environmentally-induced noise. Hardware used for building the instrument was obtained at low cost. The instrument frequency output is extremely stable over time. Analysis of this system's capabilities show this system is capable of ionic cyanide determinations in the sub-ppm range. Sensitivity is limited by poor reproducibility from the method of sampling, not by instrument capabilities.

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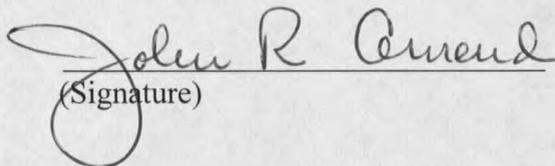
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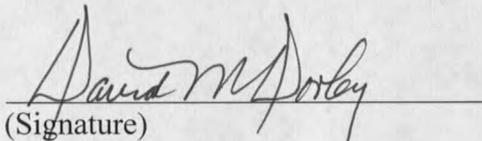
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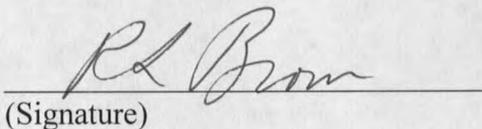
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ABSTRACT

Cyanide is present in many industrial effluents; however, standard methods of detection are often inadequate for regulating effluent waters. Piezoelectric cyanide detection as described in this paper presents an attractive alternative to the standard methods for cyanide determination due to its high sensitivity, simplicity, and lack of interference. A system was designed and built for cyanide detection. Electronic noise is eliminated by mixing two high frequency sine waves to produce a low frequency sine wave as input into a frequency counter. A reference crystal in the same environment as the sampling crystal is used to correct for environmentally-induced noise. Hardware used for building the instrument was obtained at low cost. The instrument frequency output is extremely stable over time. Analysis of this system's capabilities show this system is capable of ionic cyanide determinations in the sub-ppm range. Sensitivity is limited by poor reproducibility from the method of sampling, not by instrument capabilities.

CHAPTER 1: INTRODUCTION

Background

The US Department of Health and Human Services describes cyanide as “one of the most rapidly acting poisons” (US 1991). The Agency for Toxic Substances and Disease Registry included cyanide in their list of the “hazardous substances most commonly found at superfund waste sights and which pose the most significant potential threat to human health” (Oak Ridge National Laboratories 1989). Cyanide can be inhaled, ingested, or absorbed through the skin. Lethal oral ingestion in humans has been reported as 0.56 mg/kg and death by inhalation can occur with exposure to 90 ppm hydrogen cyanide. Long term (5-15 years) exposure to concentrations as small as 6.4 ppm of hydrogen cyanide have been reported to cause serious health problems for the nervous and cardiovascular systems (El Ghawabi 1975). In freshwater, cyanide concentrations as low as 7.85 µg/L can cause death for certain species of fish (EPA 1986).

The cyanide ion is used extensively in industrial applications including the metal finishing and mineral processing industries; consequently, cyanide and cyanide complexes appear in the rinse water, effluent, gas scrub water, and other waste waters associated with these industrial processes. Severe toxic effects of cyanide and stringent environmental regulations present a serious waste management problem for these industries. Industrial efforts for regulation and treatment of cyanide-contaminated

effluents require dependable analytical procedures which can aid in monitoring and help provide a better understanding of the water chemistry associated with cyanide-containing waste.

Industrial Use and Implications

The cyanide ion consists of one carbon and one nitrogen triple-bonded together with a negative charge; it is polar and electropositive. The water chemistry associated with cyanide is complicated due to its high reactivity. Hydrogen cyanide, also referred to as molecular cyanide or hydrocyanic acid, is a gas and has a pKa of 9.31 at 25° C (CRC 1983) and therefore is present in aqueous cyanide-containing waters at a pH below 9.3. Simple and complex metal cyanides are present in many aqueous cyanide-containing waste. Simple cyanides are compounds containing the cyanide ion and following the formula: $A(CN)_x$ or $M(CN)_x$, where A is an alkali earth and M is a transition metal. Cyanide bonds ionically with the alkali earth metals, such as sodium and potassium, to form simple cyanides. In the presence of transition metals cyanide acts as a ligand, complexing with the metals to form compounds of high stability. Complexes contain both an alkali metal and a metal, the metal being iron, chromium, silver, or others (McGivney 1985). Some examples of cyanide complexes are $K_3[Cr(CN)_6]$ and $K[Au(CN)_2]$.

The unusual properties of cyanide make it a desirable reagent for industry. Over 350,000 tons of cyanide are produced in the United States each year for industrial

applications ranging from electroplating to the manufacturing of dyes and pigments (EPA 1988).

The usefulness of cyanide and its affinity for metals is exploited by the mineral processing industry. During a process called leaching cyanide is used to bring gold and other precious metals from low-grade ores into aqueous solution. Cyanide forms a soluble complex with the gold (Equation 1):



Gold present as sulfides, arsenides or tellurides requires tank leaching to maximize gold recovery by cyanide. After the precious metals are recovered both the cyanide and the tailings go to the waste pond (Von Michealis 1985).

As with many hazardous and highly utilized chemicals, cyanide poses a waste management problem for the mining industry and others who must dispose of cyanide-containing waste. Cyanide is regulated under the Clean Water Act Effluent Guidelines for many industrial point sources such as organic chemicals, inorganic chemicals, iron and steel manufacturing, mineral mining, aluminum forming, and others (Oak Ridge National Laboratories 1989).

The role of cyanide as a complexing agent for metals not only explains its industrial benefits, but its toxicity as well. Cyanide forms stable complexes with ferric iron, causing it to bind to cytochrome oxidase, the terminal component in the electron transport chain for the mitochondria. This prohibits the enzyme's ability to catalyze the reduction of oxygen by reduced cytochrome, resulting in impairment or cessation of oxygen respiration and possibly death by respiratory collapse (Way 1984).

The EPA Water Quality Criteria has set a limit for 4-day average natural water cyanide concentrations to not exceed 5.2 $\mu\text{g/L}$ more than once every three years. For salt water this value is even lower at 1.0 $\mu\text{g/L}$ (EPA 1986). Maximum recommended contamination level for cyanide is 0.01 mg/L in drinking water; rejection for treatment of raw water supplies is 0.2 mg/L (EPA 1980). Because of the difficulties involved in detecting cyanide, the maximum recommended levels are unfortunately similar to the sensitivity limits for the EPA-recommended standard methods of cyanide determination.

Standard Methods of Cyanide Detection

EPA-recommended standard methods for cyanide determination include colorimetric, titrimetric, and electrochemical methods (including potentiometry and the use of cyanide selective electrodes). Total cyanide analysis includes all free and complexed cyanides, but only free cyanide is capable of being determined by these three methods. By known methods, complexed cyanides can be further classified as weak complexes (weak-acid dissociable), moderate complexes (cyanides amenable to chlorination) or strong complexes (Standard Methods 1989). An acid distillation process outlined by standard methods as a required pretreatment serves to break these complexes down and allow for quantification of ionic cyanide.

The EPA recommended distillation also serves as a removal scheme for a number of interferences associated with the three determination methods. Unfortunately, this treatment can further complicate the effect of interferences. Acid distillation conditions produce erroneous results from colorimetric and titrimetric methods when any of the

following are present: Sulfide, nitrate, nitrite, thiocyanate, aldehydes, ketones, and certain oxidizing agents. In addition, if fatty acids are present they will co-distill and form soaps under alkaline titration conditions. Most serious interferences are caused by sulfide as well as thiocyanate and thiocyanate complexes which decompose to cyanide upon distillation. In subsequent determination steps sulfide ions give a positive interference for cyanide-selective electrodes. Sulfide ions can be air oxidized to polysulfides which react with cyanide to form thiocyanide (Oak Ridge National Laboratory 1989).

In addition to the interference problems, the EPA-recommended standard methods of cyanide determination are time-intensive and lack selectivity and/or adequate sensitivity. For example, in a study by Goulden and co-workers the colorimetric and titrimetric method recommended by ASTM did not allow cyanide to be quantitatively recovered in concentrations below 0.1 mg/L. In an effort to automate a cyanide detection method, Goulden determined that the release of molecular cyanide from an acidified solution is a relatively slow process and the distillation equipment commonly available for automated analysis does not provide satisfactory results below 0.2 mg/L (Goulden 1972).

To circumvent these problems considerable attention has been devoted to improving the overall effectiveness of metal-cyanide complex digestion and to finding alternatives to the titrimetric, colorimetric and electrochemical determination schemes. Following is a brief outline of the effort and creativity applied to this area of analytical chemistry.

Advances in Cyanide Detection

Over the past 20 years much effort has been devoted to the improvement of standard methods or development of new cyanide determination schemes. This is a result of the difficult analytical problems associated with the standard methods and because of the demand by industry and others for an efficient, specific and sensitive method.

“Only recently has there been much interest and progress in the development of reliable and sufficiently sensitive analytical methods for the determination of free cyanide, molecular cyanide, or cyanide ions in waters containing cyanide complexes of widely varying stability. Although several methods have now been developed and published, they are still little known and apparently have been profitably employed... it has long been obvious that the total cyanide determinations made and reported routinely in the past are often insufficiently instructive, if not meaningless, as measures of water quality” (Doudoroff, 1976).

The preparative distillation procedure outlined by standard methods allows for total cyanide analysis and serves to remove the cyanide from complex matrices, but it requires one hour of strong acid distillation. In an effort to improve the efficiency of this step, sequestering agents such as EDTA (Csikai 1983), Tiron and TEP (Inersoll 1981) have been added to displace cyanide from stable cyanide complexes with varying success. One advantage of adding sequestering agents is that the pH can be kept moderate during the distillation, avoiding the dissociation of SCN^- which would otherwise give a positive interference for cyanide. In some cases the distillation time can be shortened to 1/2 hour.

Efforts have been applied to the use of UV irradiation to induce photodecomposition of the cyanide-metal complexes. Kelada successfully developed an

automated method for total cyanide analysis using UV irradiation and following with acidification and thin film distillation (Kelada 1989). Rosentreter demonstrated the efficiency of this method, documenting up to 100% dissociation for all cyanide-metal complexes except ferrous cyanide in 33 minutes exposure time (Rosentreter 1991).

Sodium hypophosphite was added to prevent photo-oxidation of the free cyanide ion to cyanate under UV conditions.

In 1984 the development of resin-based anion-exchange column allowed the use of high pH eluents, extending the usefulness of ion chromatography to anions with pKa values greater than 7.0. Cyanide had been previously difficult to analyze because it is only weakly dissociated below a pH of 9.3. With the alkaline capabilities of ion chromatography, cyanide can be effectively separated from sulfide and other anions and detected via electrochemical detection (Thomas 1984).

Another method employs the use of Chloramine-T to oxidize cyanide to cyanogen chloride which is then extracted with hexane and quantified by electron capture detection. Detection limits are 0.25 ppm (Oak Ridge National Laboratory 1989).

Recent papers have reported the use of Surface-enhanced Raman spectroscopy (SERS) for the direct detection of trace cyanide in groundwater and wastewater. Cyanide has a linear response from 100 ppm to 10 ppb, with an estimated detection limit of 8 ppb (Shelton 1994). An advantage is that cyanide can be detected in high ionic solutions such as that of groundwater.

Detection limits in the sub part-per-billion range were achieved using an indirect atomic absorption method (Rosentreter 1991). In a flow-through configuration cyanide

solutions were treated with silver and subsequent analysis for AgCN allowed for quantification of the cyanide ion.

Enzyme-based amperometric sensors have been developed for the detection of cyanide utilizing its inhibitory effect in the electron transport process. The loss of the enzyme's ability to reduce oxygen in the presence of cyanide translates to a loss of current. The catalytic activity of the enzymes is very specific for cyanide, further eliminating the effect of interferences found in other detection methods. Smit, et. al., reported the use of horseradish peroxidase in a dual-working electrode which attained a sensitivity to cyanide at sub-ppb concentrations (Smit 1990). The enzyme tyrosinase has been incorporated into an electrode which detects the presence of hydrogen cyanide in air (Rechnitz 1993).

A simple cyanide determination method using the reaction of cyanide with hemoglobin was explored (Tomoda 1991). The change in absorbance of methameoglobin due to binding with cyanide are correlated to the concentration of cyanide, with sensitivity down to 2 ppm.

Many of these methods are extravagant and costly, labor intensive, and some still suffer from poor sensitivity. Sophisticated instrumentation and expertise required for atomic absorption spectroscopy and raman spectroscopy is not always available to industry. While some techniques have marked advantages such as specificity or automation capability, there remains a need for an inexpensive, simple, and most importantly, sensitive determination method for aqueous cyanide. It is envisaged that the quartz crystal microbalance and its piezoelectric effect, as described by Nomura, Bunde

and Rosentreter, can be used to establish such a method for cyanide determination (Nomura 1980, Bunde 1993).

Quartz Crystal Microbalance

Theory

In 1880 Jaques and Pierre Curie found that when pressing or applying a mechanical strain to a crystal, an electric potential is generated from the displacement of crystalline atoms and subsequent formation of dipoles. This phenomenon was named the piezoelectric effect, using the Greek root word *piezein* (to press). The Curie brothers experimented with the converse of this effect as well, in which the application of an electric field causes a mechanical strain on the crystal (Ward 1990).

The application of an electric field normal to the surface of the crystal results in what is called shear deformation. This phenomenon results from the individual structures of the crystal being shifted as stress is applied in one direction, then the other. The electric field is confined to the area between the two excitation electrodes and causes a vibration analogous to transverse waves traveling in a string of length (L). The string resonates when the applied frequency matches one of the fundamental frequencies (f_0) which is dependent on the mass per unit length (m_l) by the following equation where S is the tension on the string (Ward 1990):

$$f_0 = (S/m_l)^{1/2}/2L \quad (2)$$

The dependency of the frequency on the mass per unit length translates to a dependency on the density of quartz, and the previous equation can be re-written to include the shear modulus (μ) and density (ρ) (Equation 3):

$$f_0 = (\mu/\rho)^{1/2}/2T_q \quad (3)$$

An increase in the crystal thickness (T_q) results in an increase in the wavelengths ($\lambda = 2T_q$), decreasing the fundamental frequency. An increase in the mass without a change in the thickness of the crystal results in an increase in mass per unit length or density, and a subsequent decrease in the fundamental frequency.

Properties of the crystal such as the angle of cut, water solubility and temperature resistance affect piezoelectric oscillation. With these properties taken into account, instrumental use of a piezoelectric crystal detector is limited to alpha crystal, and the AT-cut is used for its superior temperature coefficient and mass sensitivity (Czanderna 1984). Typical oscillation frequencies are on the order of 1 to 10 megahertz (MHz) (Bard 1991).

Saurbrey was the first to set up a series of metal deposition experiments and prove the relationship between the fundamental frequency of oscillation of the crystal and its mass (Saurbrey 1959). The change in frequency due to the coating of metal (Δf in Hz), the frequency of the quartz plate (f in MHz), the mass of the deposited coating (Δm in g), and the area coated (A in cm^2) all need to be considered (Equation 4):

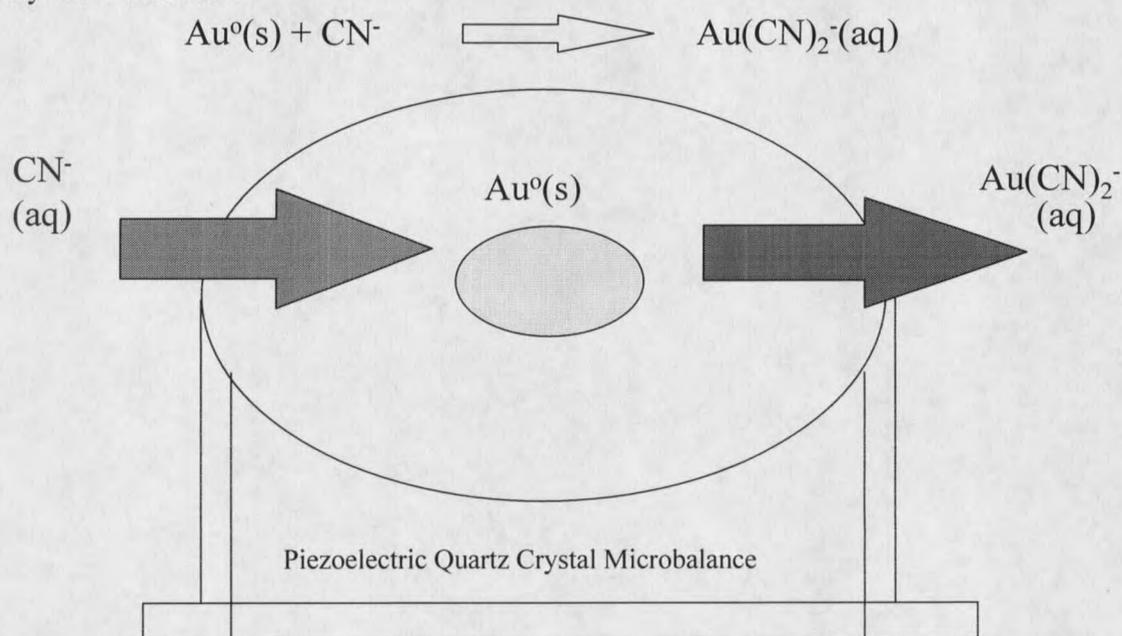
$$\Delta f = -2.3 \cdot 10^6 f^2 \Delta m / A \quad (4)$$

This equation presented is ideal, assuming any change of mass is a change in mass of the crystal itself (Czanderna 1984). According to this equation, a change in mass of 1 nanogram would result in a frequency change of 0.4 Hz for a 9 MHz crystal, or 2.6 Hz for a 15 M Hz crystal. The potential mass sensitivity of this device is therefore apparent. The now widely-used piezoelectric oscillating crystal is commonly referred to as a quartz crystal microbalance (QCM).

QCM Cyanide Detection:

Piezoelectric crystals are used almost exclusively for the detection of some mass gain or thin film deposition. An exception is the use of piezoelectric crystals for cyanide detection. A crystal plated with gold or other metal that complexes with cyanide will lose some of its mass upon exposure to cyanide by the same principle of cyanide leaching explained earlier as used in the mineral industry. This loss of plated gold translates to an increase in frequency proportional to the amount lost and; therefore, the amount of cyanide present (Figure 1).

Figure 1. Cyanide leaches gold from a gold-plated piezoelectric crystal and decreases the mass of the crystal, causing the fundamental frequency of oscillation exhibited by the crystal to increase.



In general, sampling or exposure of the crystal to cyanide is accomplished separately by dropping the cyanide solution on the crystal surface, immersing the crystal in a beaker of aqueous cyanide, or passing aqueous cyanide across the surface of the crystal in a flow cell. The frequency is monitored prior to sampling and the difference in frequency before and after sampling is considered the frequency shift due to mass loss by cyanide.

Literature Review

In 1980 Nomura and coworkers published a paper describing the application of a piezoelectric crystal for the detection of cyanide (Nomura 1980). Determination of cyanide was performed with an inexpensive single silver-plated crystal and oscillator system. The cyanide leached the silver from the silver-plated crystal by the same mechanism described earlier for gold. The frequency change was monitored by a digital counter and recorder. Since the system did not correct for temperature, the crystal, crystal holder, and oscillator were set in a thermostated air bath at 30° C.

The sampling procedure was as follows: Transfer a constant volume of 50 mL of standard solution adjusted to pH 9.3 to a beaker immersed in a water bath at 25 oC. Stir the solution at a constant rate (430 rpm) and immerse the crystal (frequency had previously been monitored) for exactly 15 minutes. Remove the crystal, wash it with water and then acetone. Set the crystal and oscillator in the air bath and measure the frequency after 1 minute.

Nomura claimed the calibration graph for cyanide concentration vs. frequency change to be linear over the range of 1×10^{-7} to 1×10^{-5} M. The standard deviation was 15.5 Hz (3.6%) for 5 determinations of 5×10^{-6} M cyanide with the same crystal. With a different crystal for each determination the standard deviation was 17.9 Hz (4%).

Interference effects were insignificant or non-existent for ions such as nitrate, perchlorate, carbonate, sulfate, aluminum, chromium, iron or ammonium. Iodide, thiosulfate and sulfide interfered by forming silver salts on the electrode. Metals such as lead (II), cadmium (II) and copper (II) and others interfered by forming stable cyanide

complexes, but most metals could be completely masked by adding EDTA to the sample solution.

In 1993 Bunde and Rosentreter (Bunde 1993) reported cyanide detection with a piezoelectric crystal in which a commercial microprocessor QCM unit was used. The commercial unit corrected for temperature and barometric pressure by subtracting the output of a reference crystal from a sampling crystal.

Bunde and Rosentreter used both gold and silver plated piezoelectric crystals and exposed the crystal to cyanide via two methods: a single-drop method and a flow cell method. The single drop method employed very small sample sizes and a 5 minute sample time. The flow cell method used a crystal mounted at 45° to the horizontal. The sample was introduced to the surface of the crystal for 15 minutes at a flow rate of 0.34 mL/min. Blank solutions (distilled water adjusted to pH 12) were run between each sample solution.

2 ppm solutions were used to test the precision of the experimental procedure. An average change in frequency was calculated to be 971 Hz and the RSD (relative standard deviation or coefficient of variation) as 3.7%. Bunde and Rosentreter claimed the precision of the system to be dependent on flow rates. For flow rates of 0.17 and 0.41 the RSD was calculated as 35% and 19.8% respectively. For use with a silver electrode the RSD was calculated as 14%.

Interference tests were performed with 100 ppm solutions. Results were similar to those for Nomura except that thiocyanate and iodide were not found to interfere with the gold plated crystals.

The cost of the commercial system used for these experiments is currently around \$7,000 (Universal Sensors price list). Fluctuations in power or other electronic noise which often interfere with high frequency electronics caused instrumental drift and instrument drift made analysis difficult. All experiments were conducted in a faraday cage, and even radiation from the lights was suspected to induce fluctuations in baseline frequency (Rosentreter).

Statement of Research Objective

The goal of this research is to design and develop a cost-effective, sensitive, stable instrument for piezoelectric cyanide detection. Construction of a dual crystal oscillating system that can be controlled with a laboratory interface and computer will be undertaken. The heterodyne principle will be used to mix the high frequency signals from the reference and sampling crystal in a manner which allows for maximum stability and correction of environmental parameters. The reference crystal will be configured to precisely gate the sampling period, in an effort to stabilize and simplify the piezoelectric system, and allow for the use of the interface counter without introducing additional error into the output. Experiments will be conducted to assess the stability and extent of correction of this instrument and the capability for cyanide detection. These experiments include the following: monitoring the output as a baseline over time; comparing temperature response of dual crystal system vs single crystal system; designing a sampling protocol and assessing noise induced from the protocol; determining the precision of the system for a constant treatment with cyanide; and calibrating the system output with cyanide concentration.

CHAPTER 2: INSTRUMENT DEVELOPMENT

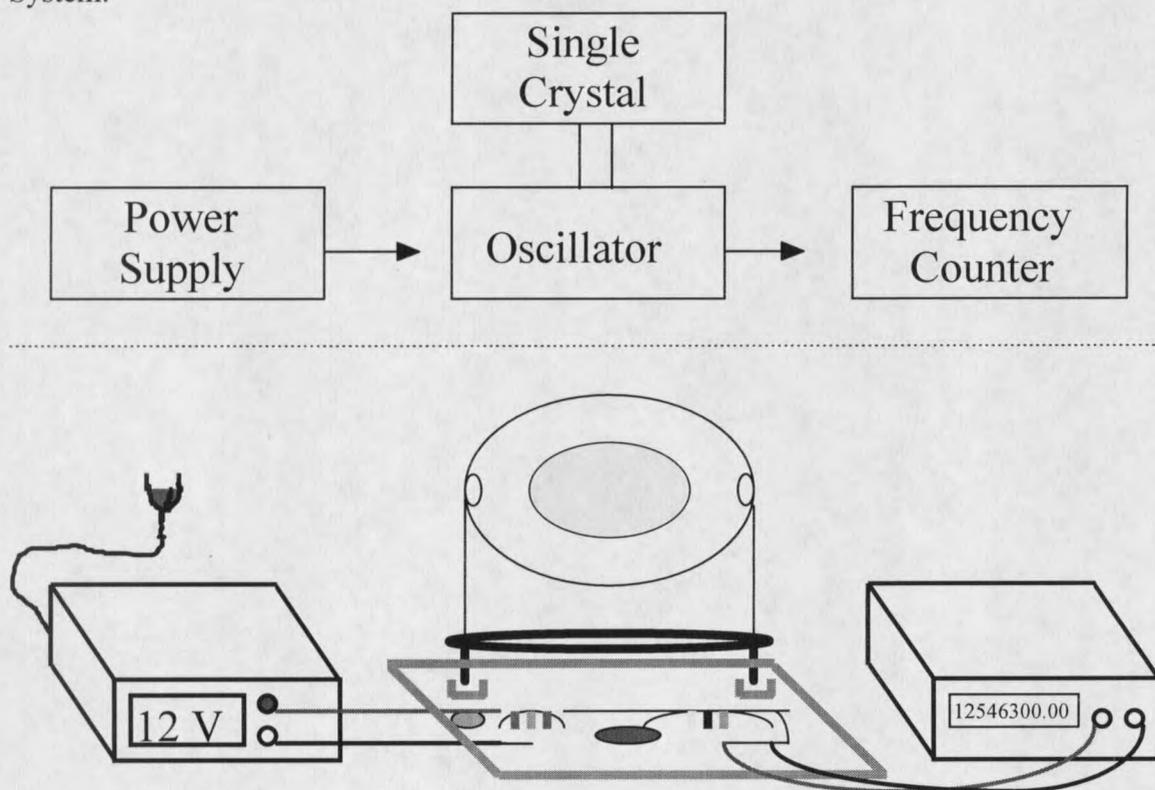
This chapter outlines some problems we encountered in developing a piezoelectric system. Two major modifications were made to the initial system and to instruments used previously for piezoelectric cyanide detection. The first is the use of the heterodyne principle for subtracting external noise. Second is the use of the reference crystal as a gate for the frequency counter.

Initial Attempts

Single Crystal

Initially we conceived and built the simplest working piezoelectric device (Figure 2). This is the type of system used by Nomura for cyanide detection (Nomura 1980), consisting of a crystal and an oscillator which applies a voltage to the crystal, and a frequency counter to monitor the oscillating crystal. A thermostated air bath to contain the apparatus was not available and was unwieldy to use in the possibility of a field situation.

Figure 2. Block Diagram and Pictorial Representation of Single Crystal Oscillating System.



The frequency was counted either by a computer interface or by a conventional frequency counter. The conventional frequency counter was much more stable than the interface counter, drifting as little as 10 Hz out of 10 MHz over 120 minutes. The signal, however, appeared to be very susceptible to noise and it was cumbersome to record data manually.

The frequency output when using the interface counter was erratic and unpredictable, even the direction of drift after turning on the instrument was not constant. A stable baseline could not be achieved; standard deviations for 30 minutes were as high

as 17 Hz, and overnight experiments produced drifts in the order of 100 Hz. Following is a graph of mean frequencies measured with the interface after doing such things to the crystal as unplugging it, washing and drying it, exposing it via a drop on the surface to 5 and 10 ppm cyanide for 3 minutes (Figure 3). The mean values are from monitoring the frequency counts for a few minutes and determining a mean value. The recorded frequency is a few KHz because of limitations with high frequency counting by the interface and electronic manipulation of the high frequency signal. Standard deviations are in the order of 8 to 13 Hz.

The frequency output shifted up to 100 Hz (data point 14) just from drifting. Wetting and drying the crystal produced shifts in frequency that varied by a standard deviation of 217 Hz. When looking at signals around 1000 Hz for exposure to cyanide this background noise seemed unacceptable. Furthermore, the frequency shift did not double as would be predicted from the relationship defined by Sauerbrey (Equation 1) for sampling with 5 and 10 ppm cyanide. A stable baseline and a sampling procedure which produced greater signal to noise ratio must be achieved to make a useful system.

