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# Automated Controlled-Potential Coulometer for the IAEA

by

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**Abstract**

An automated controlled-potential coulometer has been developed at the Savannah River Site (SRS) for the detection of plutonium for use at the International Atomic Energy Agency's (IAEA) Safeguards Analytical Laboratory in Siebersdorf, Austria. The system is functionally the same as earlier systems built for use at the Savannah River Site's Analytical Laboratory.

All electronic circuits and printed circuit boards have been upgraded with state-of-the-art components. A higher amperage potentiostat with improved control stability has been developed. The system achieves electronic calibration accuracy and linearity of better than 0.01%, with a precision of better than 0.001% and a temperature stability of 0.001% per degree Celsius. Plutonium measurement precision and accuracy better than 0.1% has been demonstrated.

This coulometer features electrical calibration of the integration system, electrolysis current background corrections, and control-potential adjustment capabilities. These capabilities allow application of the system to plutonium measurements without chemical standards, achieving traceability to the international measurement system through electrical standards and Faraday's constant. The chemist is provided with the capability to perform measurements without depending upon chemical standards, which is a significant advantage for applications such as characterization of primary and secondary standards. Additional benefits include reducing operating cost to procure, prepare and measure calibration standards and the corresponding decrease in radioactive waste generation.

**Introduction**

This system is designed to measure the concentration of plutonium samples in the 5 to 10 mg range with an accuracy of +/- 0.1 %. The latest system built for the IAEA has achieved accuracy in the +/- 0.05% range. Work is in progress on a cell assembly designed for 1 mg samples. Two systems have been built for the SRS Analytical Laboratories Department, and one for the International Atomic Energy Agency (IAEA). The primary uses include: accountability measurements, process control, non-proliferation measurements, and calibration of plutonium measurement systems which are not directly traceable to the National Institute of Standards and Technology (NIST). SRS has also applied the system to the measurement of 20 to 40 mg neptunium samples with comparable reliabilities.

The primary purpose of the SRS controlled-potential coulometer is to make highly accurate plutonium and (neptunium) measurements directly traceable to NIST. Samples in the 5 to 10 mg

range are measured in a nitric or sulfuric acid solution. Although enhancements have been made to each of the four systems fabricated to date, the basic block diagram is the same.

The main system controller is interfaced to a precision voltmeter, pulse generator, frequency counter, digital-to-analog converter, printer and custom coulometer modules. The modules include two potentiostats, one digital integrator, a supply module, and an automation module. The automation module contains the electrical calibration circuit and interconnecting circuits and relay. This module interconnects the other coulometer modules with the controller, voltmeter with the potentiostats, and the potentiostats with the cell assembly or the internal electrical calibration circuit. One potentiostat controls the reduction of plutonium and the other controls oxidation. All samples are pre-reduced to the  $Pu^{3+}$  oxidation state. The oxidation potential is then applied to the cell. By integrating the electrolysis current with respect to time during the oxidation of plutonium to  $Pu^{4+}$  process, and applying Faraday's law, a direct relationship to the amount of plutonium in the sample can be determined. Since the reaction rate decreases exponentially taking an unacceptable length of time to complete, the control potential is accurately adjusted to achieve background current at about 99.8% completion of the sample reaction. The Nernst equation is then used to calculate the remainder of sample to be oxidized.

The two systems used at SRS have demonstrated accuracy of better than 0.1 % over a period of 10 years. Results have been documented in a report issued by the developers (ref. DOE Report DP-1751 issued in June 1988). Using the latest system built by the SRS developers, the IAEA Laboratory in Seibersdorf, Austria has achieved accuracy as good as +/- 0.05%.

The SRS system is based on work originally completed at the New Brunswick Laboratory (NBL) in the early 1980s. When one of the key developers (M.K. Holland) left NBL and joined SRS in 1984, work began on the fabrication of a new generation system. The first system at SRS was put into operation in 1986, a second followed in 1988, a third was built for Rocky Flats in 1989, and the latest system built was for the IAEA which was delivered in 1995. A process of continuous improvement over the last 14 years in the design and fabrication methods has evolved. The resulting system is the most accurate and reliable controlled-potential coulometer in the world. The interest in the system throughout the world has been clearly documented.

The SRS system uses state-of-the-art electronics and advanced printed circuit board technology. The digital integrator module, for instance, has documented stability and accuracy better than 1 part in 100,000 or 0.001%. The potentiostat module is capable of delivering over 200 mA current while maintaining an extremely stable control potential. The system is resistant to electronic noise and easy to maintain. The overall benefit of the advanced electronic design combined with integral electronic calibration capability is its ability to be electronically calibrated. The calibration which converts counts from the integrator to coulombs is directly traceable to the NIST. The electronic calibration is based upon the measurement of voltage, current and resistance. Since the calibration is automatic, it can be run anytime when actual sample measurements are not being performed. The calibration factor used in the sample measurement automatically corrects for any drift in the electronics. The method of calibration prevents the need for chemical standards and has documented accuracy of +/- 0.05%. This number is key since the international target value for accuracy of plutonium accountability measurements is 0.1 %.

In addition to the accuracy, the SRS system has been shown to have minimal down time and excellent long term stability. This is based on over 10 years of operational experience at SRS. The software is menu-driven and provides all of the required report generation capability. Highly accurate results

have been achieved at SRS and by the IAEA showing the flexibility of the system. With minimal training, the expert staff at IAEA have been able to operate and maintain this system.

Due to the versatility of the hardware and software, the system could be adapted to other coulometric measurements. The system, while automated, can be used in a manual mode which could be more applicable to university research. A university professor had expressed interest in a manual system in the late eighties. At the time, lack of funding and availability of SRS staff for non-SRS mission activities prevented supporting this application. Since the primary need for accurate plutonium measurements is associated with the nuclear material accounting, processing and/or stabilization, the primary customer base is very limited.

## Hardware

### System Controller

Hewlett Packard Model R-362 Computer with IEEE-488 interface and General Purpose Input/Output Card (GPIO).

### Custom Coulometer Modules

NIM Bin - EG&G bin modified back-plane wiring for interconnection of coulometer modules.

Potentiostat Module - Upgrades have been made to the Potentiostat module. The module includes two printed circuit boards, the control amplifier card, and the switching and load card. The basic functional blocks of the circuits have not changed, however, all components have been upgraded. The control amplifier card supplies current to the cell during electrolysis while maintaining a constant stable control potential. The output capability of the circuit is 1 Amp, however, the cell assembly and the size samples being measured limit the current to under 200 mA. The control amplifier card uses a 4 -layer configuration that minimizes signal routing, reduces signal crosstalk, and eliminates ground noise.

A variety of power and signal sources are used by the Potentiostat Module for control, power, and signal needs. Module system power, +/- 12V and +/- 24V are provided by the NIM Bin power supply. Automated system power, +5V, is provided by a separate modular power source. This controls the relay system throughout the coulometer modular system. The potential is supplied by a 6V DC floating supply. The Data Acquisition Voltage Supply is used in the 0-1 and 0-10 V DC range to automatically adjust the otherwise control potential on the potentiostat modules. The DAC voltage signal is fed to the non-inverting input of the operational amplifier to vary the offset between the amplifier and the instrument ground. The cell current monitor is supplied by a 4.8V battery powered circuit. Each source is completely isolated from other sources.

In series with control potential circuit is a precision 50 ohm resistor. The oxidization current generates a voltage proportional to the cell current for use by the Integrator Module. The Integrator Module converts the analog signal to digital form. This A/D conversion isolates the analog signal from the Integrator system.

Digital Integrator Module - The digital integrator module has been upgraded with all new components. The main component of this module is the voltage-to-frequency converter

circuit board. This board utilizes multiple floating voltage sources to eliminate ground noise. The result is an extremely stable frequency output. The input range is 0 to 10 Volts corresponding to a frequency output, 0 to 100,000 Hz. The frequency output is stable and accurate to less than 1 count. Precision 0.01% resistors and state-of-the-art op amps are used in the amplifier circuit.

The digital integrator is composed of two voltage-to-frequency converters and a quartz crystal oscillator. The signal from the potentiostat that is to be integrated and a small offset signal are supplied to Variable Frequency Controller (VFC) #1. Only the offset signal is supplied to VFC #2. The offset signal is supplied by a 1.5V DC D-cell battery. Through op amp divider and summing circuitry, the signal and offset signals are supplied to the VFCs for A-D conversion. The frequency signals from the VFCs and crystal oscillator are supplied to the frequency counters for accumulation. The voltage-to -frequency card uses a 4 -layer configuration that minimizes signal routing, reduces signal crosstalk, and eliminates ground noise.

The board uses multiple floating voltage sources to eliminate ground noise. Modular power is supplied by  $\pm 15$ V power source provide by the Automation Module. The digital system is isolated from all external analog signals by a 5V DC-DC converter power system in the digital integrator. The output digital signals are routed to the frequency counters as discussed earlier. This system uses the earth ground that is isolated from the power grounds.

The alignment of the digital integrator provides accurate and stable frequency counts for data accumulation. This calibration method ensures that the V-F conversion is 10,000 counts per 1V. The alignment includes setting the full scale and offset of the two voltage-to-frequency converters. In addition, the accuracy of the 10.000 kHz clock signal for the integrator must be verified (and adjusted if required). [This 10.000 kHz clock signal is generated by a 200.000 kHz crystal oscillator and a divide-by-20 circuit.] The signal is generated with a calibrated voltage source and then verified with a calibrated multimeter. Frequency counts are measured with a calibrated frequency counter. The following list contains typical calibration results. Calibration is performed from 0-10 V with 1 V increments. The frequency value is the signal plus the offset where the offset is constant. Offset voltage is the battery voltage divided by 10.000.

#### Typical Calibration Results (Table 1)

Battery = 1.587122 V

Clock = 9.999987 kHz

Calibration Signal (V)	Offset (V)	VFC #1 Frequency) (kHz)	VFC #2 Frequency) (kHz)	Calibration Factor (VFC#1-VFC#2)/ (CS)
0.00000105	0.1587002	1.587122	1.587122	-----
1.000002	0.1587002	11.587266	1.587122	10.00012
1.999993	0.1587002	21.586954	1.587122	9.99995
2.999977	0.1587002	31.58683	1.587122	9.99998
4.000024	0.1587002	41.58724	1.587122	9.99997
5.000013	0.1587002	51.58724	1.587122	10.00000

6.000009	0.1587002	61.58725	1.587122	10.00001
6.999997	0.1587002	71.58707	1.587122	10.00000
8.000001	0.1587002	81.58696	1.587122	9.99997
8.999994	0.1587002	91.58669	1.587122	9.99996

Once aligned, the coulometer generates high precision electrical calibration measurements. Typical data from consecutive groups of ten calibration measurements taken over a 24-hour period:

Typical Calibrations Measurement over 24 Hours (Table 2)

Calibration Factor <u>Microcoulombs/count</u>	Relations Standard <u>Deviation, N=10</u>
2.01305	0.002%
2.01305	0.002%
2.01303	0.001%
2.01306	0.001%
2.01306	0.002%
2.01307	0.001%

Automation Module -The primary function of the automation module is to receive the output of the instrument controller via its GPIO card. Based upon the SPIO logical signal, mercury-wetted relays connect the potentiostats with either the sample measurement cell or with high-precision 100-ohm calibration resistors. Addition relays direct desired voltages to the DVM based upon the SPIO signal.

Supply Module -The supply module consolidates and isolates power supplies used in the other coulometer modules.

Peripherals

Counters

There are 4 Hewlett-Packard Universal Counters which are accessed through the Hewlett-Packard Interface Bus (HP-IB). Commands are sent to the counters to set them up, start them counting in totalize mode, and reset them to zero. The counters are read without stopping so that they continue counting without interruption.

Digital Voltmeter

The Hewlett-Packard digital voltmeter is accessed through the Hewlett-Packard Interface Bus (HP-IB). The voltmeter is set-up and read by the controller.

D/A Converter

Commands are sent to the D/A converter using the Hewlett-Packard Interface Bus (HP-IB).

Pulse Generator

Commands are sent to the Pulse Generator to generate pulses for general timing purposes using the Hewlett-Packard Interface Bus (HP-IB).

## Results and Discussion

The Savannah River Site has provided a controlled-potential coulometer and cell-assembly system for plutonium measurements. The system was delivered and assembled in June 1995, by J.V. Cordaro, T. Fields, and M.K. Holland. Since delivery, evaluation has been directed by Georges Jammet of the Safeguards Analytical Laboratory (SAL) staff. Preliminary tests involved the measurement of iron standard solutions as a plutonium surrogate. As part of the POTAS Task following plutonium introduction, M.K. Holland returned to SAL for collaborative evaluation of measurement system performance on 10-mg plutonium aliquots. The combination of measurements made by the SAL staff, shortly before the collaborative evaluation, and the following individual measurement results obtained during this evaluation, indicated that a measurement reliability of better than 0.10% had been obtained using electrical system calibration (based upon Ohm's Law and Faraday's constant):

100.01%
100.03%
100.07%
100.02%
100.04%
100.07%
<u>100.09%</u>
Means 100.05%

RSD% 0.03%

In addition to demonstrating plutonium measurement reliability on 10-mg plutonium aliquots, the alignment of system components and the methodology for on-going demonstration of calibration tractability were reviewed.

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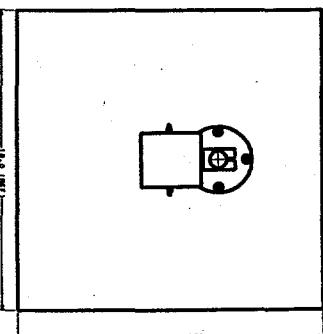
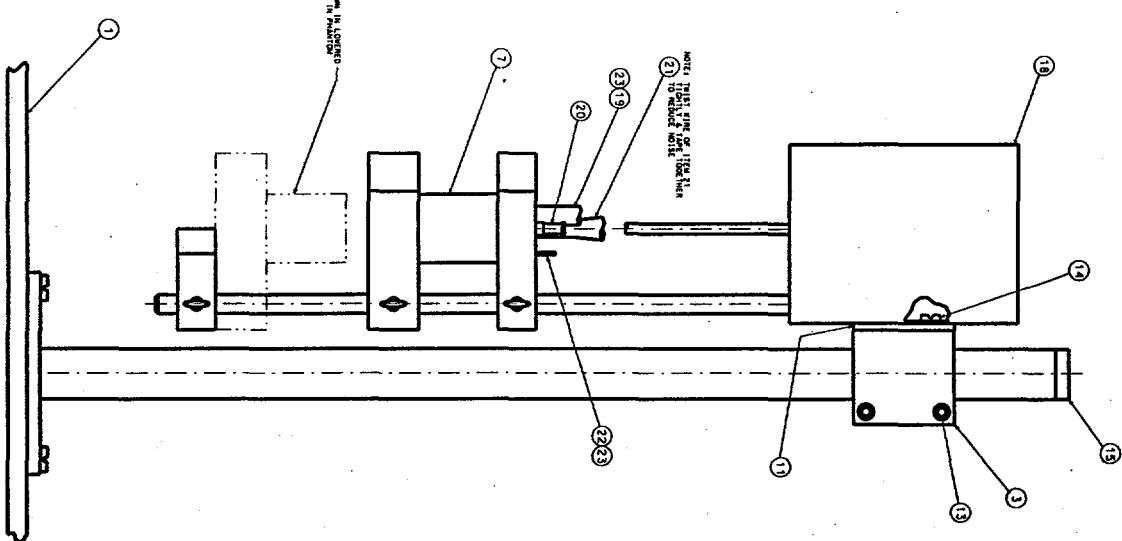
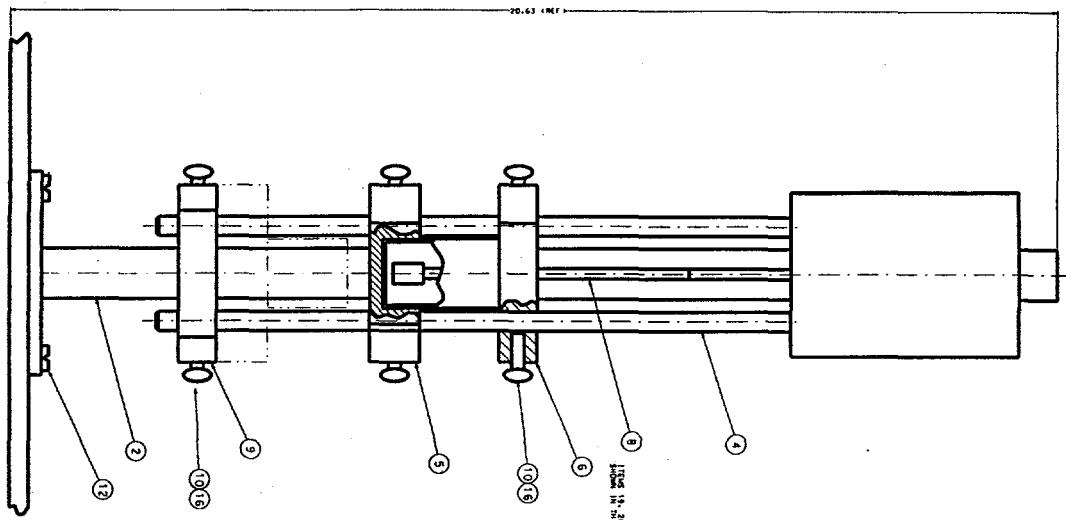
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## Appendix A

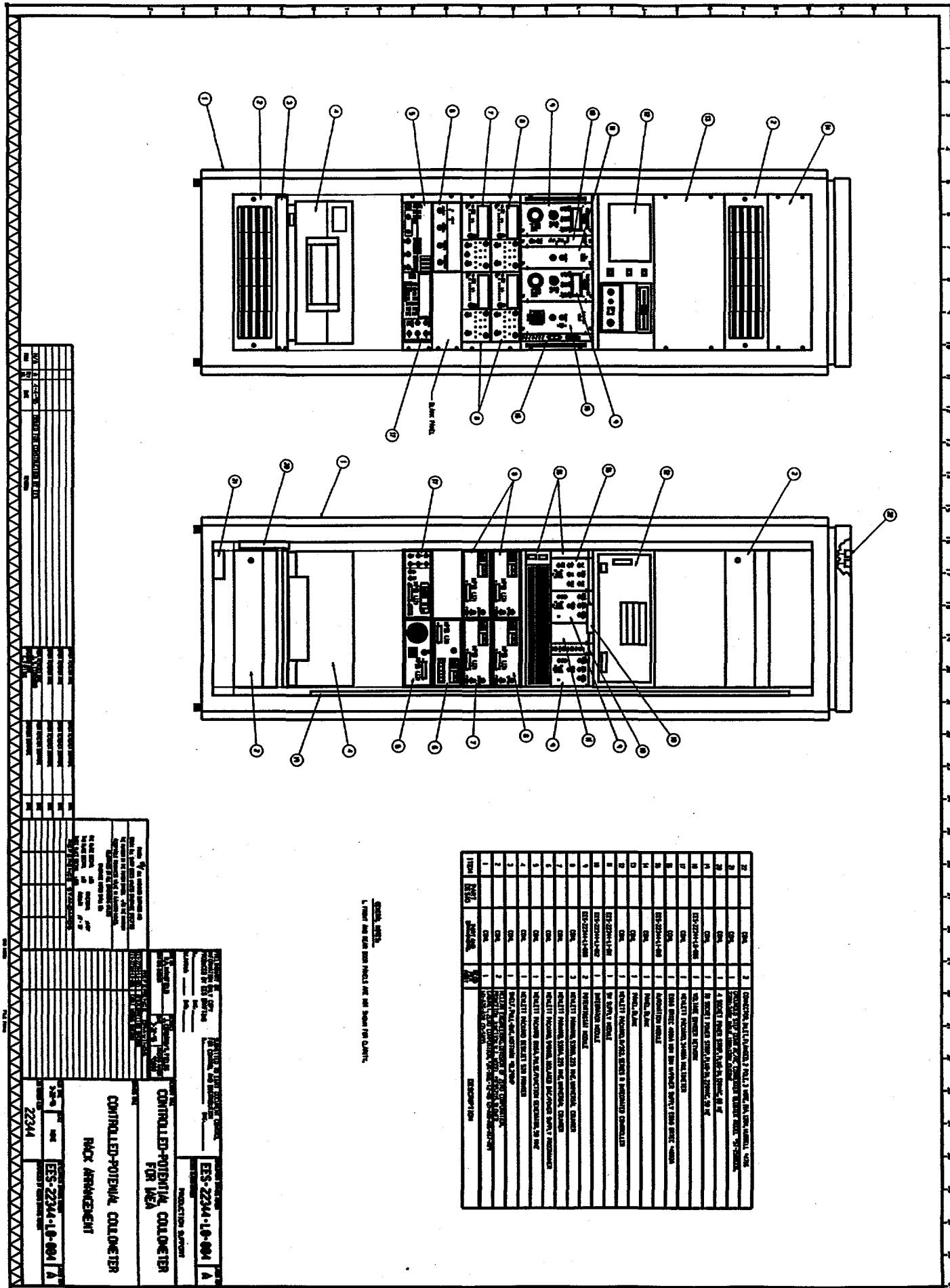
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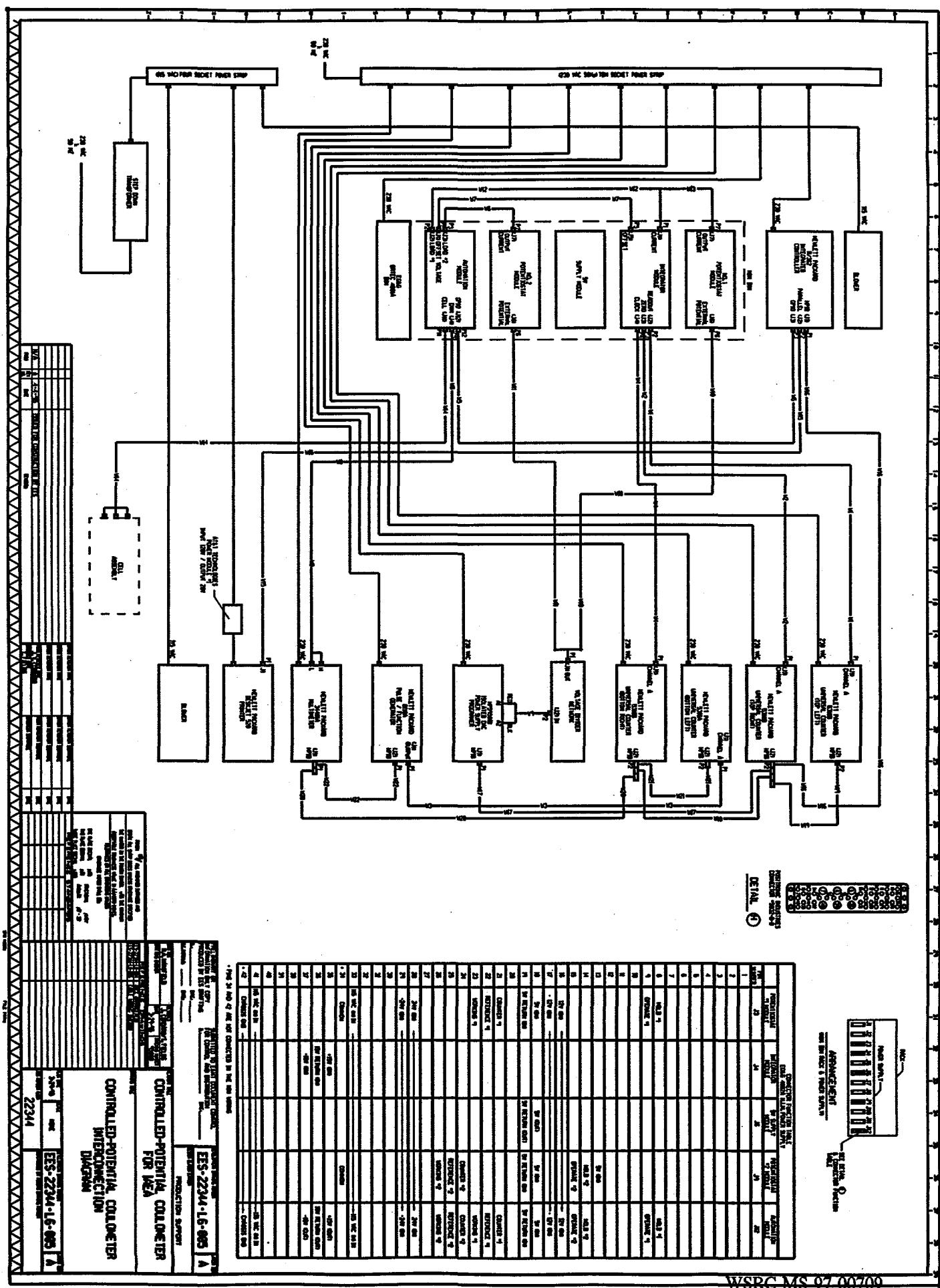
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2. EES-22344-L0-004      Controlled Potential Coulometer for IAEA
3. EES-22344-L6-005      Controlled Potential Coulometer Interconnection Diagram
4. EES-22344-LC-013      Controlled Potential Coulometer
5. EES-22113-LC-017      Potentiostat Module Control Amplifier Card
6. EES-22113-LC-008      Integrator Module Voltage to Frequency Card -Schematic
7. EES-22113-LC-014      Automation Module Driver/Interface Board

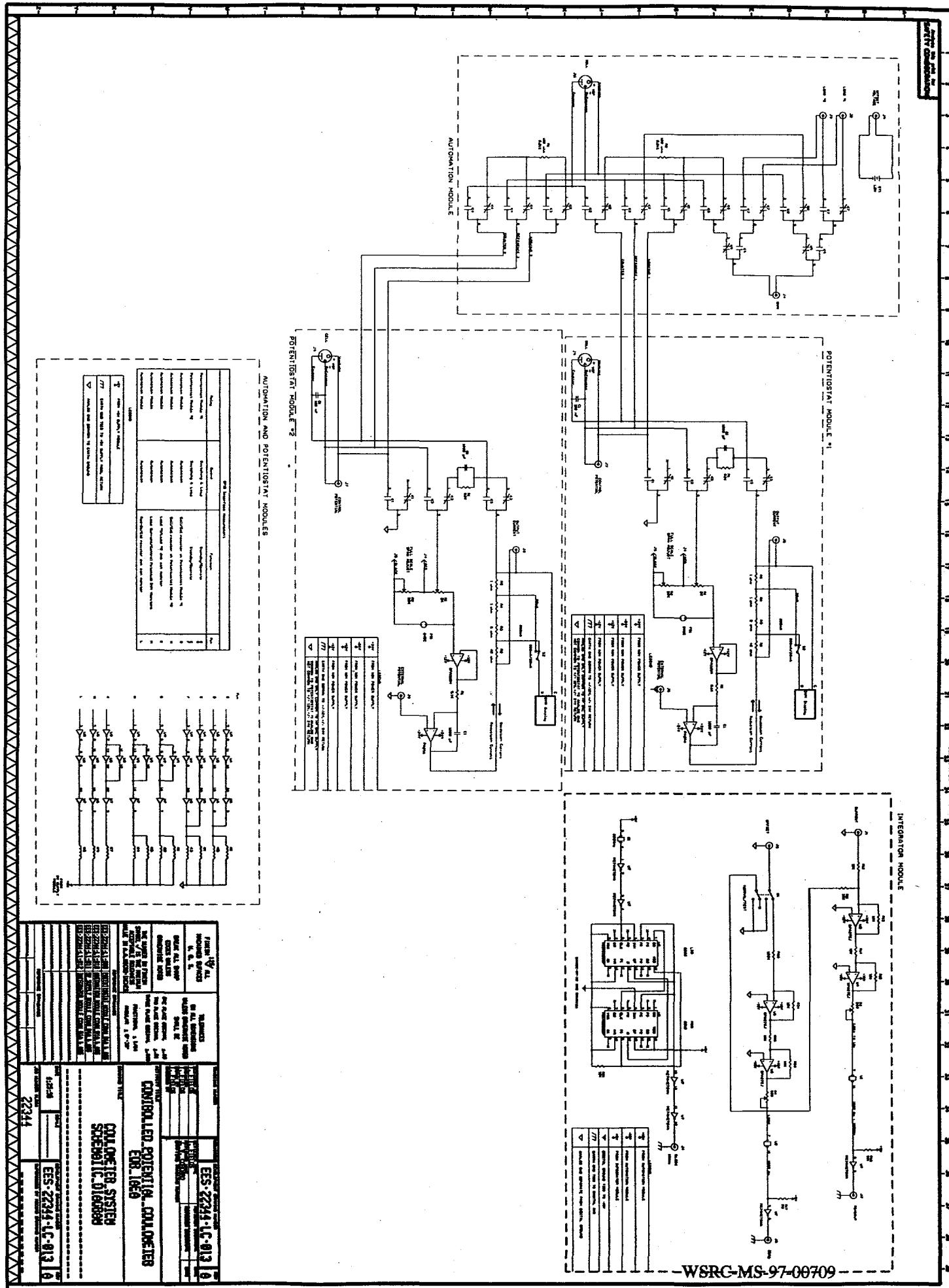


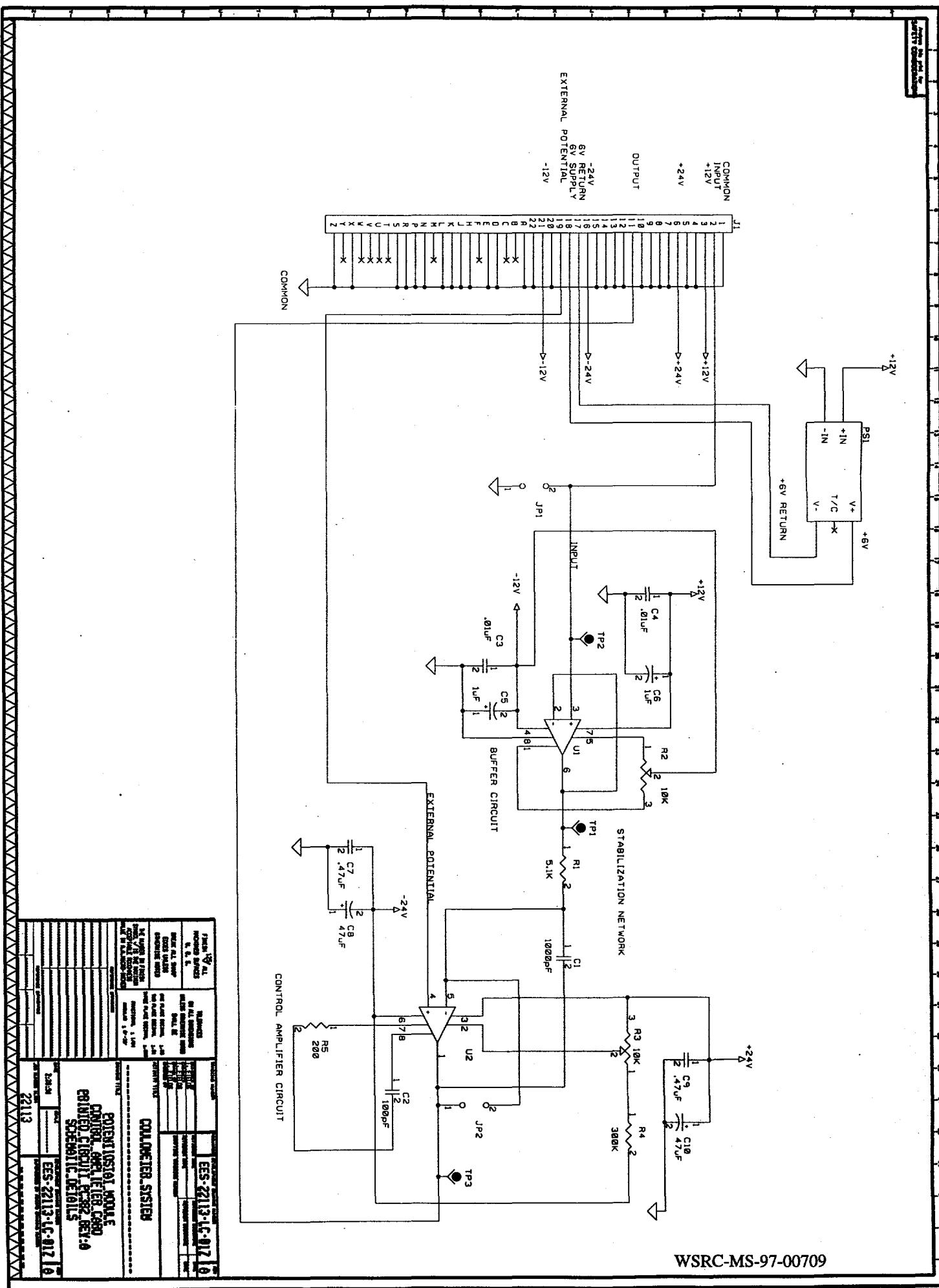
## MECHANICAL ASSEMBLY

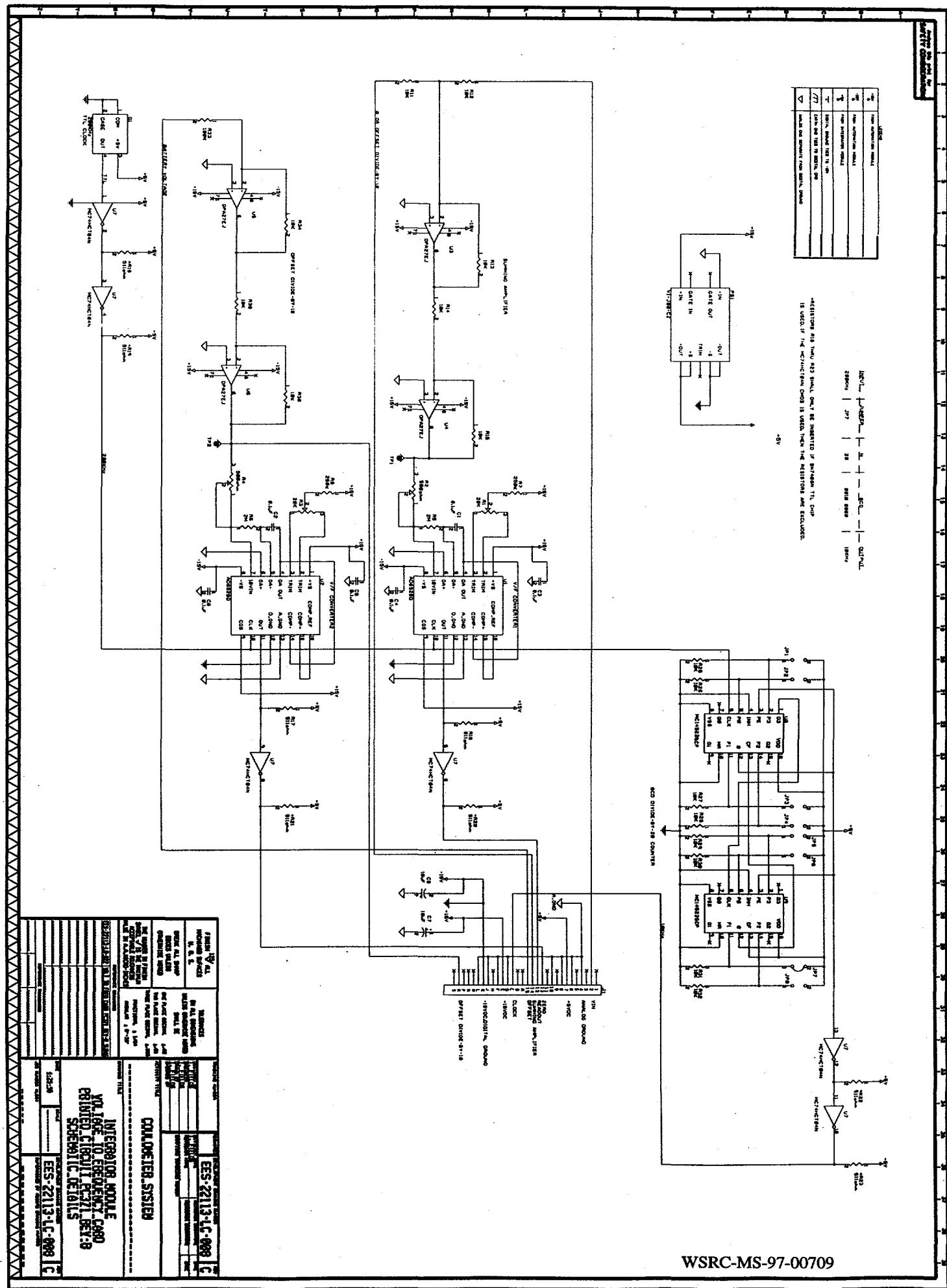
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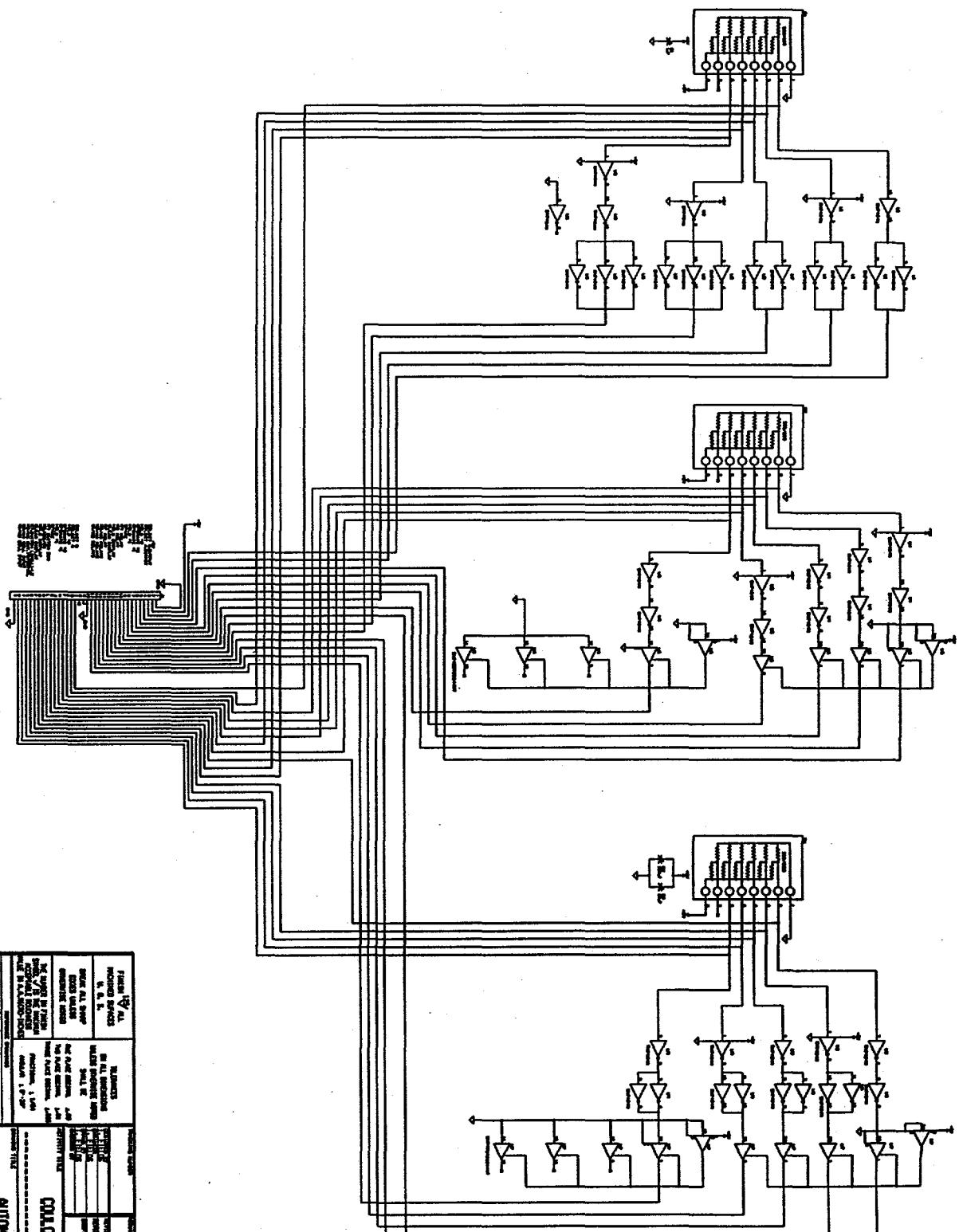








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AUTOMATION MODULE DRIVER INTERFACE BOARD PRINTED CIRCUIT BOARD SCHEMATIC DETAILS	
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REV	0
DATE	05/01/96
DESIGNER	ES-22113-CC-014