

NOAA/ESRL Safety Basis for Custom Radioactive ECD Ovens
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Version 1.2

1.0 Introduction

1.1 Define Purpose and Use of Custom ECD Ovens. NOAA is involved in world-class research on ozone depleting, climate or greenhouse, and air quality trace gases that are all important to the health and well being of the citizens of the United States. Large depletions of stratospheric ozone can cause increased incidents of fatal skin cancer. Increases in the greenhouse gases can cause more suffering through increased numbers of heat strokes in individuals and changes to climate that may not be reversed easily. Increases of atmospheric trace gases resulting in air pollution can cause more heart and lung problems for American citizens. NOAA, along with NASA, is responsible for producing an assessment of stratospheric ozone depletion every 3-4 years by the 1990 Clean Air Act. NOAA data on these climate gases were included in the report of the Intergovernmental Panel for Climate Change (IPCC), which shared the 2007 Nobel Peace Prize with former Vice President Al Gore.

The electron capture detector (ECD) is one of the most sensitive detectors made for atmospheric trace gases containing oxygen, sulfur, fluoride, chlorine, bromine, and iodine atoms. When the ECD is coupled to a gas chromatograph (GC) to separate trace gases from air, this detection method (GC-ECD) is unique for detecting low atmospheric levels of trace gases in the parts-per-billion (ppb, 1 part in 10^9) and parts-per-trillion (ppt, 1 part in 10^{12}) ranges. For example, our detection limit for sulfur hexafluoride, a greenhouse gas used in the distribution of electrical power, is 100 parts-per-quadrillion (ppq or 1 part in 10^{15}). This fantastic sensitivity is result of the efficient production of ionizing radiation that leads to electron capture or sensitive chemical ionization created by the Nickel-63, beta source in the ECD. The non-radioactive ECD-mode of a commercial photo-ionization detector does not come close in sensitivity for the halocarbons and many other trace gases, so it not an option for research now. NOAA/ESRL scientists are responsible for measuring over 50 trace gases that are involved in international agreements, including the Montreal and Kyoto Protocols.

NOAA/ESRL began using commercial ECDs in custom-made gas chromatographs in order to save space and weight in field applications. Instruments used to make measurements from balloons and aircraft must be small and lightweight. Research on how to develop small, reliable GC's with multiple ECD detectors carried over to NOAA's surface sampling programs in which multi-detector GC's were built for use at remote field sites. Further, because these measurements required extremely good measurement precision, NOAA/ESRL scientists began constructing research-grade instruments that exceeded the capabilities of commercial instruments.

1.2 Design Aspects of Commercial ECD ovens. We use commercial electron capture detectors, but we redesign the detector's oven and disconnect it from the commercial column oven. The manufacturers specifications and requirements for their ECD operation are defined from their instrumental manuals [Shimadzu, 1982; Hewlett Packard, 1985;Valco, 1991]. All detectors, except the Shimadzu ECD, can be operated at

maximum of 400 °C (see Table 1). The Shimadzu must be operated no higher than 350 °C. We need to operate most of our detectors between 330 and 400 °C to achieve maximum sensitivity for atmospheric concentrations of the halocarbons, sulfur gases (SF₆, COS), carbon monoxide, methane, hydrogen, and nitrous oxide. Some

Table 1 Manufacturer’s Specifications and Requirements for their ECDs.

ECD model	Nickel-63 (mCi)	Amount of Ni ⁶³ (mg)	Max. Temp (° C)
Valco	5	85	400
Shimadzu	10	170	350
Hewlett Packard (HP)*	15	250	400
Shimadzu	10	170	350
Hewlett Packard (HP)*	15	250	400

*Agilent Technologies is the successor company after HP was split up and reorganized in 2000. The HP and Agilent detectors are almost identical.

detectors are operated at lower temperatures (60-250 °C) for a few specific purposes (e.g. atmospheric organic nitrates, CFC substitutes, etc).

As a example of the maximum temperature requirement, the Hewlett Packard manual goes further and states “In the extremely unlikely event that both the oven and the ECD-heated zone should go into thermal runaway (maximum, uncontrolled heating in excess of 400°C) at the same time, and that the ECD remains exposed to this condition for more than 12 hours, take the following steps: (1) After turning off the main power and allowing the instrument to cool, cap the ECD inlet and exhaust vent openings. Wear disposable plastic gloves and observe normal safety precautions. (2) Return the cell for exchange following the directions included with the form general license certification (HP Pub. No. 43-5954-7621, HP part number 19233-90750).

But the manual goes on to state, “even in this very unusual situation, radioactive material is unlikely to escape the cell. Permanent damage to the Nickel-63 plating within the cell is possible, however, so the cell must be returned for exchange”. Valco’s manual states that “it has been demonstrated that Nickel-63 is chemically stable at temperatures up to at least 500 °C, which exceeds the maximum operating temperature of the ECD 140BN” [Valco 1991]. Control of ECD temperature is the most critical parameter in terms of safety. Measures to control and limit ECD temperature vary among commercial instrument manufacturers. Hewlett-Packard and Agilent monitor the temperature of the nearby column oven to make indirectly sure that the ECD does not exceed 400 °C. Both Shimadzu and Valco use a second temperature sensor to monitor the ECD so it does not exceed the maximum allowable temperature. Once the maximum temperature threshold is met, the ECD heater is disabled resulting in ECD cooling.

1.3 Design Aspects of NOAA/ESRL Custom ECD Ovens.

NOAA custom GC's include ECDs installed in custom-made heated zones. These zones consist of a metal enclosure containing the ECD, a resistive heating device, a temperature sensor (RTD), insulation, a thermal relay (also called a manually resettable thermostat), and a temperature controller. Drawings are provided of the inside assembly of the NOAA/ERSL custom ovens in Appendix A. The design permits holes for heater cartridges and RTDs. Drawings of the outside can which is sealed at 1 atmosphere during the ECD use is shown in Appendix B. The temperatures of the ECDs are maintained by off the shelf Proportional-Integral-Derivation controller (PID controller) that can maintain a desired temperature to within +/- 0.1 to 0.2 °C at a set temperature of 350 °C. The PID controller is commonly used in critical industrial control systems. The PID controller corrects for the error between a measured temperature and a set-point for the detector temperature by calculating a correction to the measured temperature. The proportional value calculates the reaction to the current error, the integral value calculates the reaction to the sum of recent errors (a history), and the derivative error calculates the reaction based on the rate at which the error has been changing. A tuning algorithm will calculate the optimum value of each PID parameter to maintain constant temperature. Not all of the commercial detectors listed in Table 1 use PID control for temperature, which we feel is a safety improvement other those without complete PID control.

Safety Features

2.1 Radiological Risks. The radiological risks can be defined, as near term and long term, in terms of the possibility of developing cancer later. The risks for commercial ECDs are the same as our custom ECD oven gas chromatographs. There are MSDS sheets from various manufacturers of Nickel-63 sources that detail fundamental physical parameters, human exposure limits, and what to do during an accident (See Appendix C). The MSDS gives emergency information on a source in a breached or open cell, mark the area with Radioactive Danger Area Tape, and stop all activities near the damaged source until Radiation Safety Officers (RSOs) arrive. Agilent has defined the near term radiological risks from a 15 mCi of Nickel-63 plated on a platinum foil for various interactions with the source by human activity (See Appendix D). In summary, Agilent has calculated that "persons working with an unshielded source of 15 mCi of Nickel-63 at a distance of 16 cm from the source would require continuous exposure of 1,471 hours to obtain the annual public dose rate of 100 mrem". Agilent calculates "A person receives a level of less than 0.00001% of the values listed below when the source is within an unopened detector housing."

2.2 Non-Radiological Risks. Nickel itself is a toxic metal that can cause problems in the human body, however the amount of nickel present in the ECDs is at milligram levels (see Table 1). In a diluted amount (0.00001%) from the sealed source, nickel poses no risk to humans.

2.2 Venting of ECD exhaust. Valco recommends venting the ECD exhaust out a fume hood, window, or outside vent. HP and Agilent recommend attaching a short vent line from the ECD exhaust. They recommend checking gas flows with this line. Shimadzu has no information on venting. Our understanding from venting the exhaust is more for contamination from high concentrations of samples rather than normal exhaust of the ECD. Since we are measuring trace quantities of common atmospheric gases, we vent the exhaust away from the user.

2.3 Safety features of the NOAA/ESRL Custom ECD ovens. According to the manufacturer's manual, the Valco and Hewlett Packard ECD's temperature must not exceed 400 °C, and the temperature of the Shimadzu must not exceed 350 °C. We have triple redundancy to prevent the ECD's temperature from exceeding their manufacturing operating limits. First, we have an "off-the-shelf" manually resettable thermostat that turns off the heater current when the temperature of the top of a can on the ECD oven's temperature exceeds a temperature limit (50, 75, or 90 °C). The outside temperature trip point of the thermostat is selected based on the ECD type, insulation, and its location in each instrument. Second, each "off-the-shelf" PID temperature controller has an electronic shut off of the heating circuit when the temperature sensor of the ECD (high temperature RTDs) goes into a failure mode. Third, the PID temperature controllers can monitor the rate of the temperature gradient changes too much in a certain period of time (called "loop break"). If the RTD fails and reads a nonsense value, then the heater circuit will open and allow no current to the heater. The original manufacturer only has double redundancy on their gas chromatographs, so we are exceeding the manufacturer's number of safeguards with one of each category of mechanical, sensor failure, and software (rate of temperature change) override failsafe.

3.0 Operation and Maintenance

The procedures described here pertain to a specific type of ECD heated zone in a cylindrical metal "can" defined as the custom ECD oven. This is the most common type of heated zone and is used in all but two of our operational custom GC applications. The exceptions are two ECD ovens used for low temperature detection (90° C) of organic nitrates in the atmosphere. Their ECD oven is constructed differently, where the wattage of the heater is limited to operations well below 400 °C. These procedures are similar to those we would apply to other types of heated zones, or cans, but there will be slight differences depending on the instrument configuration. None of these differences would be significant in terms of radiation safety.

3.1 Assembly

Assembly of ECD ovens ("cans") is described in the Chromatograph for Atmospheric Trace Species (CATS) manual for Shimadzu and Valco ECDs. Briefly, the procedure involves connecting 1/16" stainless steel tubing from the three ECD ports (inlet, outlet, and makeup) to bulkhead connectors on the inside of the can lid. Electrical connections are soldered to the anode and cathode wires on the ECD (Appendix C and D). The anode

is connected to an SMA connector which serves as the electrical feed-through to the front face of the can. The cathode is connected to a grounding point inside the can or to the SMA connector. The ECD itself is mounted inside the can using a triangular mounting plate, or by using the 1/16" tubing to form a semi-rigid mount. Two halves of an aluminum collar with 1/4" holes along the axis are mounted around the body of the ECD and used to hold the RTD and the resistive heater. The RTD and heater can also be mounted into the ECD body. A 1/16" purge line is connected to one port on the can lid. The other purge port is left open. The purge flow consists of 3-5 cc/min nitrogen and serves to keep the interior of the can free of oxygen to reduce oxidation of the electrical connections at high temperature. Whether or not there is flow or not through the ECD is not a radioactive safety issue. The electrical connections for the heater and RTD are wired to a feed-through connection on the lid of the can.

After all connections have been made, 40-psig nitrogen is plumbed to the ECD inlet with the other ports capped. Snoop (soap and water) is used to test for gas leaks at the three ECD ports and at the bulkhead connections on the can lid. If leaks are found, fittings should be tightened or replaced until no leaks are present. The ECD is then wrapped with insulation and inserted into the can. The can lid is then attached with machine screws. The can is then labeled with the ECD model, serial number, and radioisotope caution label.

The ECD can be tested in either a GC or on the bench-top. The thermal relay is tested by applying heat to the face using a heat gun, while monitoring the electrical contacts with a digital voltmeter. The contacts should move to open circuit at the correct temperature. Reset the thermal relay using the manual reset button, and wire the relay through the heater cartridge and install the relay on the face of the can. The temperature control system can now be tested. The can is purged of air using nitrogen prior to heating. The ECD is plumbed with appropriate carrier gas (N₂ or Ar/CH₄) and the can should be connected to a PID temperature controller. Consult the CATS manual for proper settings on the controller. The sensor type (typically a 100-Ohm RTD) needs to be entered into the controller software. Check that the RTD reads a reasonable value at ambient temperature. Then set the operating temperature to 100 °C and observe the ECD temperature. It should increase slowly and begin to control as it reaches the set point. If the temperature does not control, proceed with troubleshooting. If the temperature is controlled but oscillates more than a few tenths of a °C, the PID parameters of the temperature controller may need to be tuned. Ultimately the temperature controller should be stable to within ± 0.1-0.2 °C. Consult the CATS manual for typical settings and consult the controller manual for instructions on tuning. If the controller is functioning correctly, set the temperature set point to the desired operating temperature and observe the heating cycle. If the controller operates correctly at the desired temperature, the ECD is ready for use.

3.2 Routine Operation

ECDs assembled in custom-made heated zones should perform well for several years without maintenance. Typical procedures for routine checks on GCs operated at long-

term monitoring sites include a daily check on ECD operating temperature and other GC parameters (see CATS daily check sheet). Engineering data, including ECD temperature, are logged by software on varying time scales. These data are used primarily for troubleshooting purposes.

3.3 Troubleshooting

A procedure for troubleshooting the control of the heated zone temperature is outlined in the CATS manual. Briefly, this procedure involves checking the thermal relay or thermostat, checking the resistance of the heater cartridge, and the resistance of the RTD. If these systems appear to be operational, then a spare temperature controller can be installed in place of the suspect controller. Here one must be careful to initialize the controller with the same parameters used in the old one. If the controller is not operating correctly and the problem is not obvious, the heater circuit should be disabled by disconnecting the circuit at the thermal relay or disconnecting the controller until the problem is solved. A faulty or suspect heated zone should not be left “powered up”.

In the unlikely event that the ECD overheats without tripping the thermal relay or thermostat (defined as ECD temperature exceeding the manufacturer’s rated temperature, other than in a transient manner), the power to the ECD heater should be disconnected, either by turning the GC off or by disabling the heater circuit. If the system was logging data at the time of suspected overheat, check the data record to examine the recorded ECD temperature. If the record shows a sustained temperature more than 5% higher than the maximum allowable, the ECD should not be used until a radiation leak is ruled out. Contact the Deputy Radiation Safety Officer and inform him/her that you would like to test an ECD for radiation leakage. Use a wipe test kit and return the kit to the Deputy Radiation Safety Officer for analysis. Following a wipe test, close the access doors of the GC and place “Caution” tape around the instrument until the wipe test results are known.

If the wipe test results indicate a radiation leak, the ECD should be considered hazardous. Follow the instructions in section 3.6 “*Replacing an ECD that has failed a wipe test*” to remove the entire can from the GC. Contact the Deputy Radiation Safety Officer for instructions on how to package the ECD for shipment to Boulder. The package should be labeled as hazardous and kept in a locked location prior to shipping. If the ECD is located at 325 Broadway, Boulder, inform the Deputy Radiation Safety Officer and arrange to have the can removed from the instrument and returned to the manufacturer. See Section 3.6 if the unit is not in Boulder, Colorado.

If the initial wipe test of the ECD exhaust is negative, reconnect the power and follow the trouble shooting procedures to check the operation of the thermal controls. The ECD should not be operated until the cause of the overheating has been determined and addressed.

3.4 Maintenance

The most common reasons for replacing an ECD are 1) poor performance (poor sensitivity or electronic noise, 2) failure of the RTD and 3) failure of the heater unit. Due to the demand for high precision, ECDs are typically not replaced without good reason.

3.5 Replacing an ECD that has not failed a wipe test

The ECD and the can lid should, in most cases, be considered a functional unit. The ECD and the can lid should be kept together. This way, the tubing and electronic connections to the can lid will remain intact, and the labeling will stay with the ECD. The following instructions are also in the CATS manual. To remove the ECD, reduce the controller set point temperature or disconnect the relay and allow the ECD to cool to room temperature. Disconnect all tubing and cap the inlets. Disconnect the electrical connection. Remove the thermal relay and the screws that attach the can lid to can base. Gently pull the ECD and lid away from the rest of the can. Installation of a new ECD attached to a can lid is basically the reverse of the above.

In rare cases the ECD may need to be removed from the can lid. This procedure is basically the reverse of the assembly procedure. However, gloves should be worn for this procedure since it will expose surfaces that are “upstream” of those regularly wipe tested. If the ECD is removed from the can lid, a radiation caution label should be attached to the ECD.

3.6 Replacing an ECD that has failed a wipe test

If the ECD is located in the field, the entire can (lid and body) should be removed from the GC, if possible. This will limit exposure to internal surfaces that might be contaminated. It is required that you wear gloves for this procedure. Turn off the power to the GC and allow the ECD to cool to room temperature. Disconnect all tubing to the ECD and cap the inlets. Disconnect the electrical connections and remove the thermal relay. Remove the mounting bolts from the can and remove the can from the GC. Place the entire can in a box and mark with caution tape. Place the box in a locked drawer or cabinet and contact the Deputy Radiation Safety Officer for instructions on how to return the ECD to Boulder.

4. Shipping Documentation.

ECDs may be shipped as an excepted radioactive instruments and articles (Appendix E – 49 CFR 173.424), on commercial passenger aircraft under the UN2911. Please see appendix F - 49 CFR 173.421 for more information on shipping.

5. Summary.

The biggest concern for the operation of commercial ECDs is to ensure that the temperature does not exceed its maximum operating temperature. The custom ECD

ovens are made as safe as possible with two to three layers of redundancy to the temperature controllers. The exhaust ports of the ECDs must also be wipe tested every 6 months to assure that the source is not leaking at a level less than 0.005 microcurie (μCi). There will be authorized users of ECDs at NOAA/ESRL and these users are on the license. There are also secondary users that operate the instruments on a day to day basis, and require less training than an authorized users. At the NOAA/ESRL sites, there is a Radiation Safety Officer and two Deputy Radiation Safety Officers. All correspondence between the NRC and NOAA will be conducted with the NOAA/ESRL Radiation Safety Officer or designate (typically the deputies). An ECD safety PowerPoint slide course has been given to all users including warehouse people, scientists, and employees at the field sites (See Appendix G). More formal training is in progress at this time. The NOAA/ESRL RSO will make sure that all users have completed ECD Safety Training, maintain inventory of all sources, and make sure that wipe test are performed every six months on operational instruments.

References:

Shimadzu [1982], Gas Chromatograph GC-Mini 2 with Electron Capture Detector, Instruction Manual, Shimadzu Corporation, Analytical Instrument Plant, Kyoto, Japan, part #221-20502A, pp. 46.

Valco [1991], Model 140BN Electron Capture Instruction Manual, Valco Instruments Co, Inc. (VICI), Houston, Texas, USA pp. 41.

Hewlett Packard [1985], HP5890A Gas Chromatograph Reference Manual Volume II, Section 15, Hewlett Packard, Inc. Palo Alto, California, USA, part#05890-60300.

List of Appendices.

Appendix A NOAA/ESRL custom oven inside can adapters for heater and RTD.

Appendix B NOAA/ESRL custom oven outside can.

Appendix C MSDS for Nickel-63

Appendix D Radiation Hazard of Agilent Technologies ECD Cell

Appendix E 49 CFR 173.424 Excepted packages for radioactive instruments and articles.

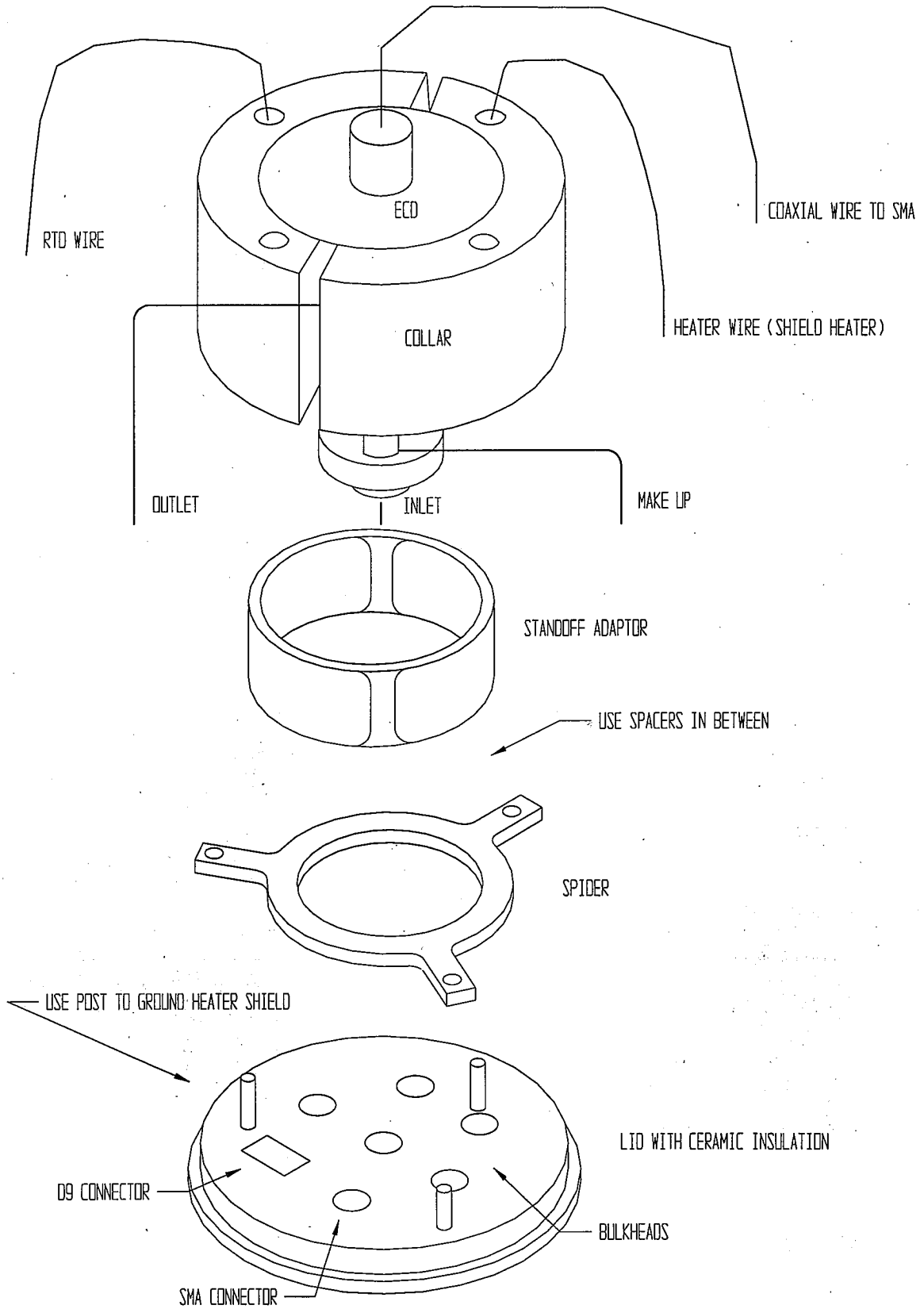
Appendix F 49 CFR 173.421 Additional requirements for excepted packages containing Class 7 (radioactive) materials.

Appendix G Powerpoint training for ECD safety.

Appendix A to NOAA/ESRL Safety Basis for Custom Radioactive ECD Ovens

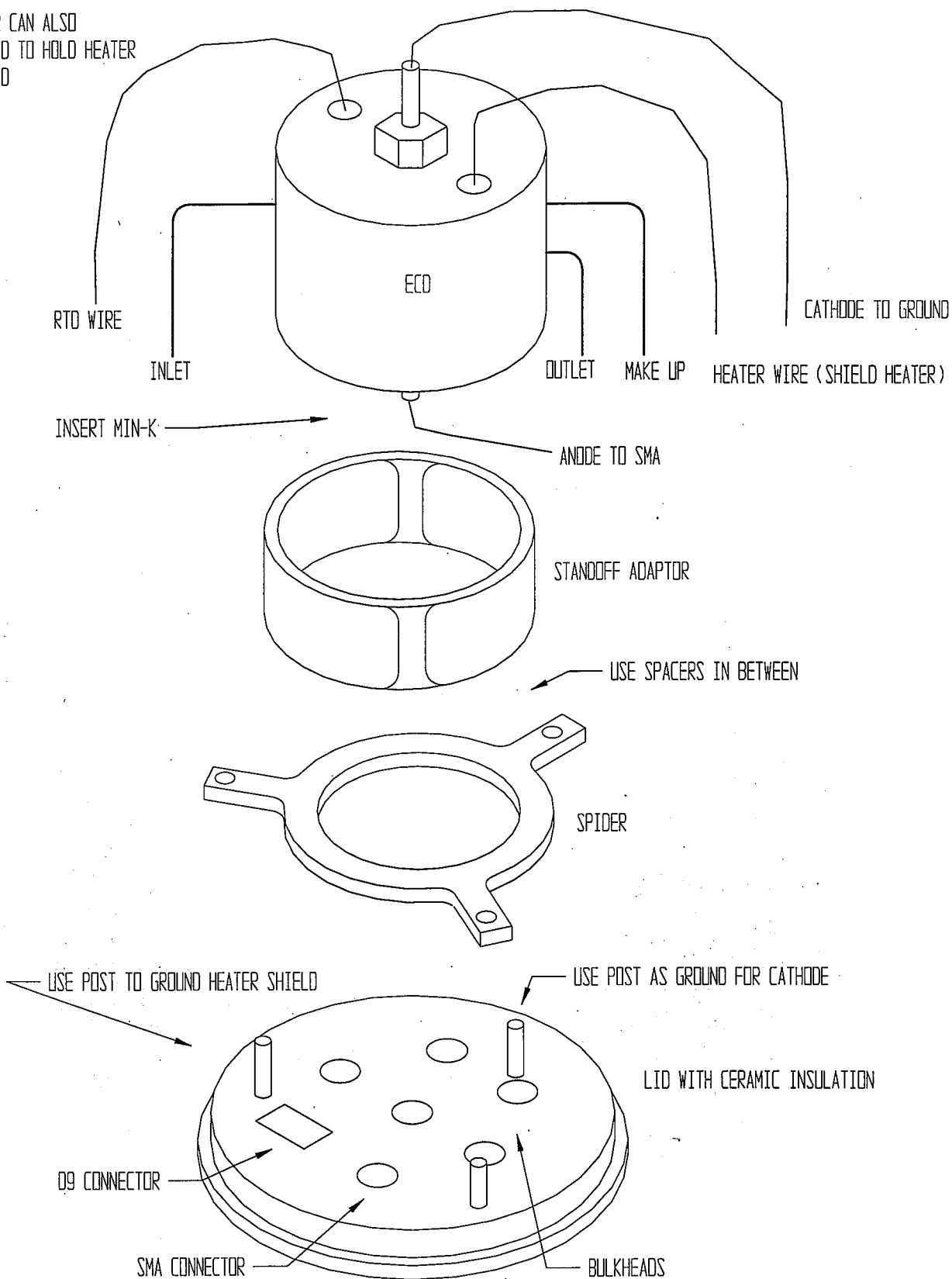
NOAA/ESRL custom oven inside can adapters for heater and RTD.

SHIMADZU ECD ASSEMBLY

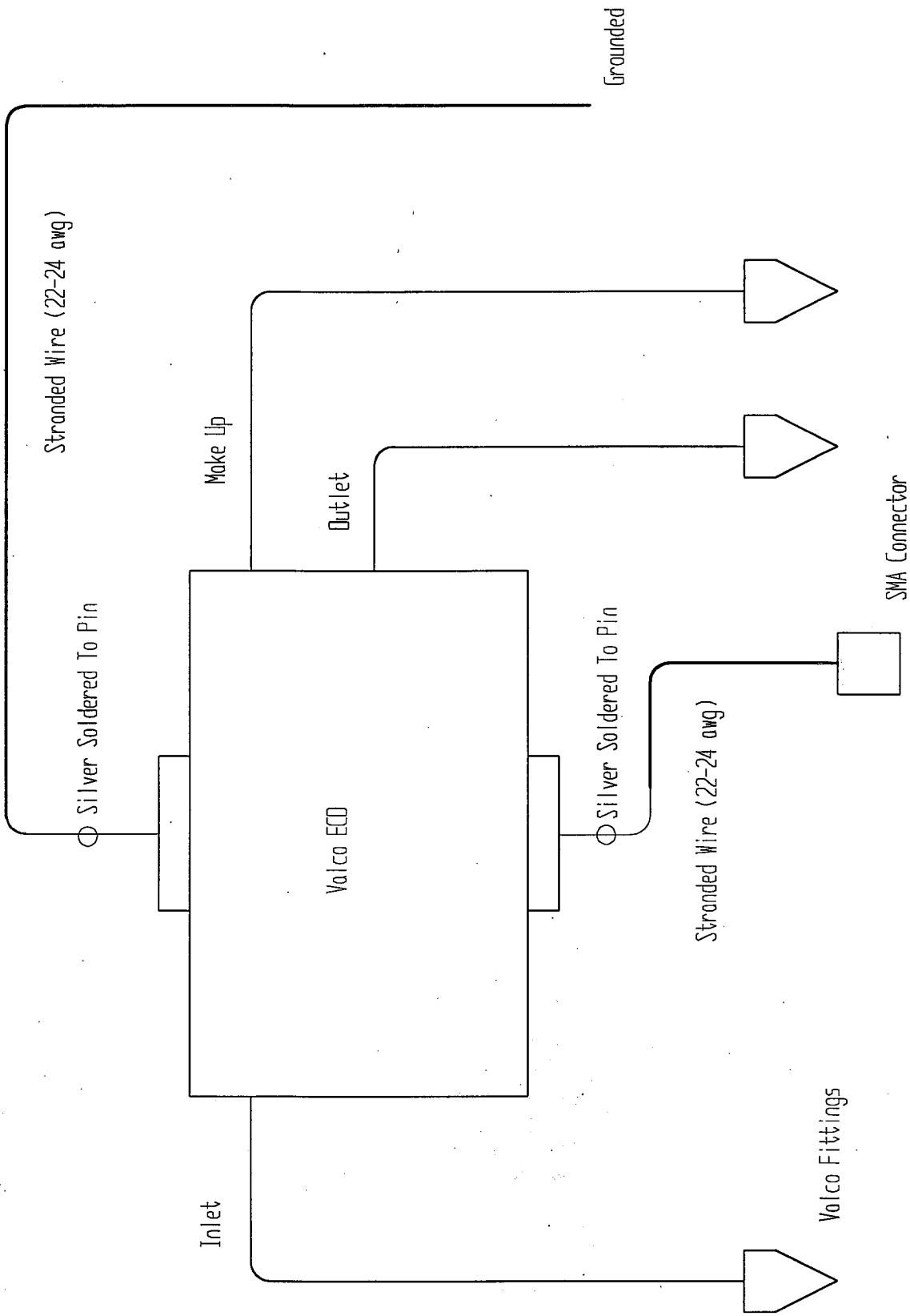


VALCO ECD ASSEMBLY

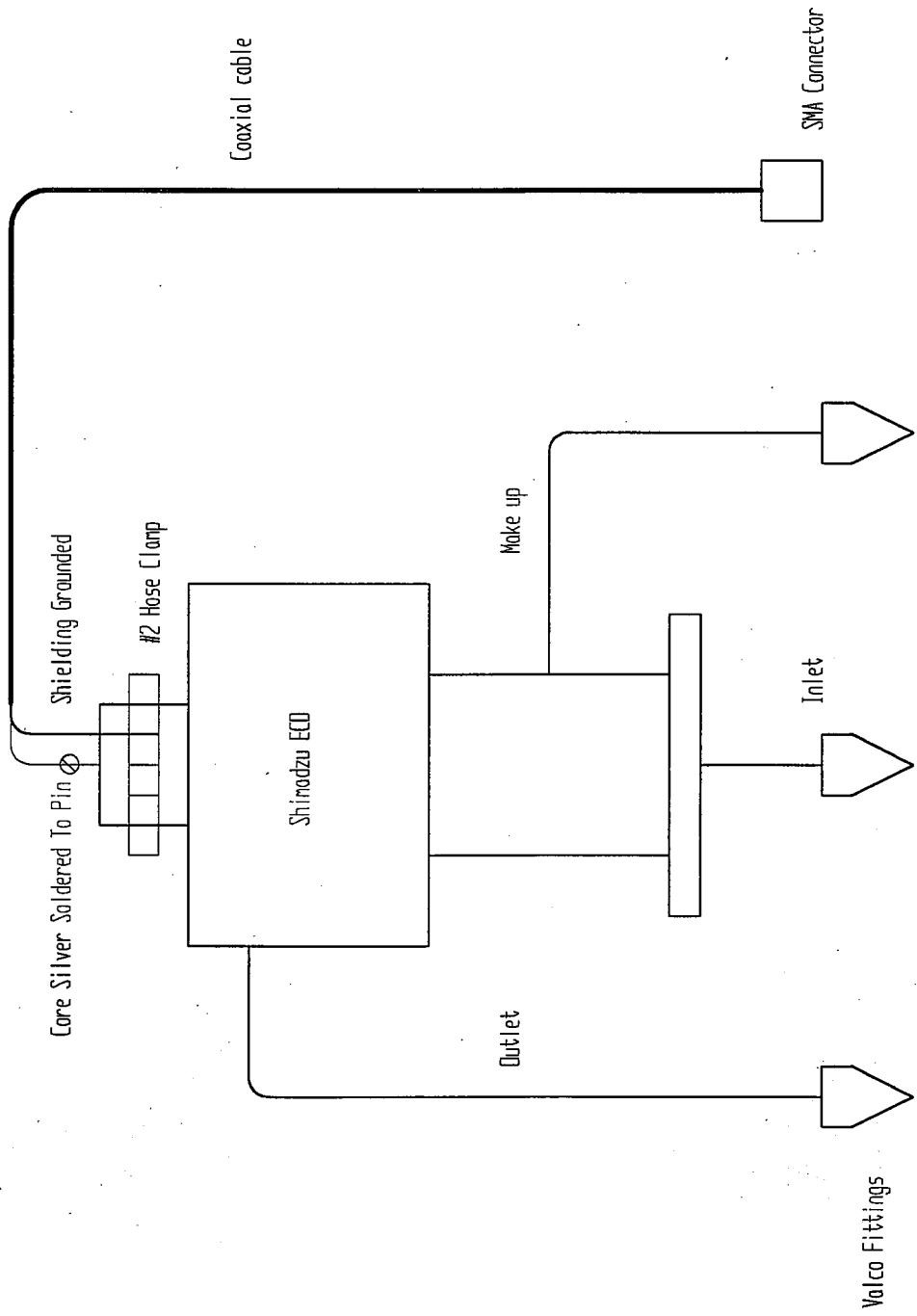
COLLAR CAN ALSO
BE USED TO HOLD HEATER
AND RTD



VALCO ECD SCHEMATIC

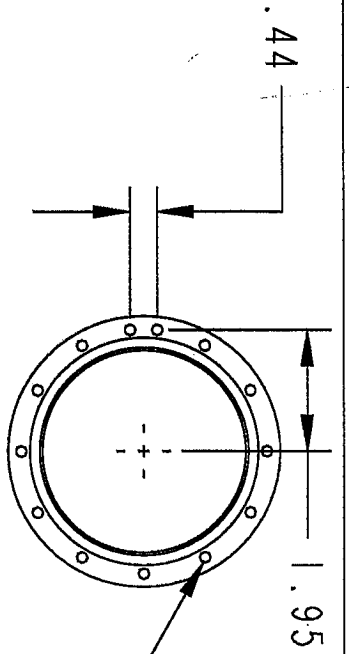


SHIMADZU ECD SCHEMATIC

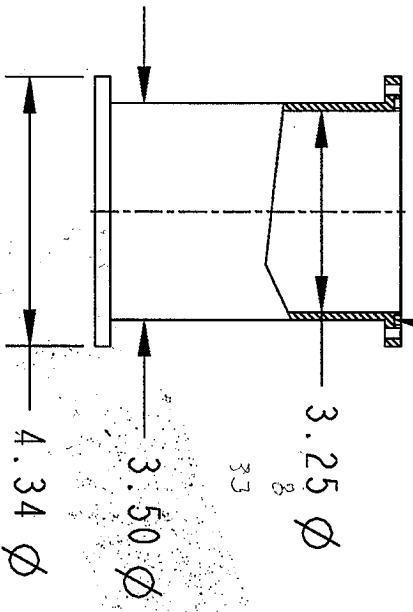
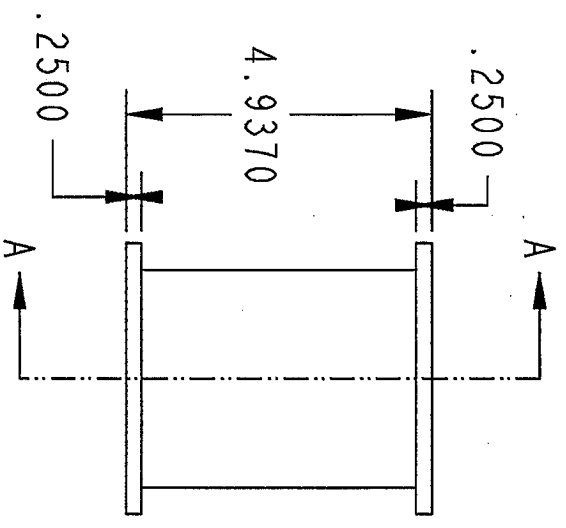


Appendix B to NOAA/ESRL Safety Basis for Custom Radioactive ECD Ovens

NOAA/ESRL custom oven outside can.

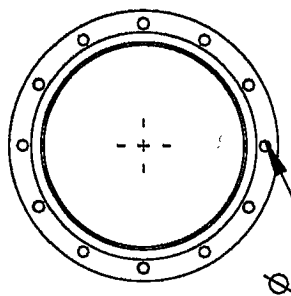
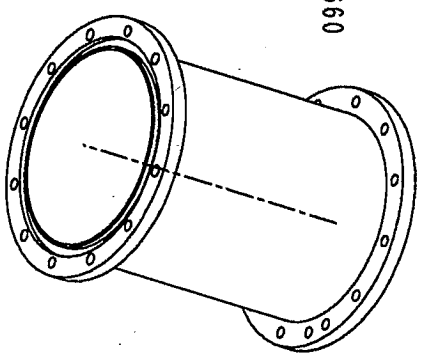


#8-32 HELICOIL 13PLCS
11 EA Ø3.925 BC 30° INC
2 EA AS SHOWN



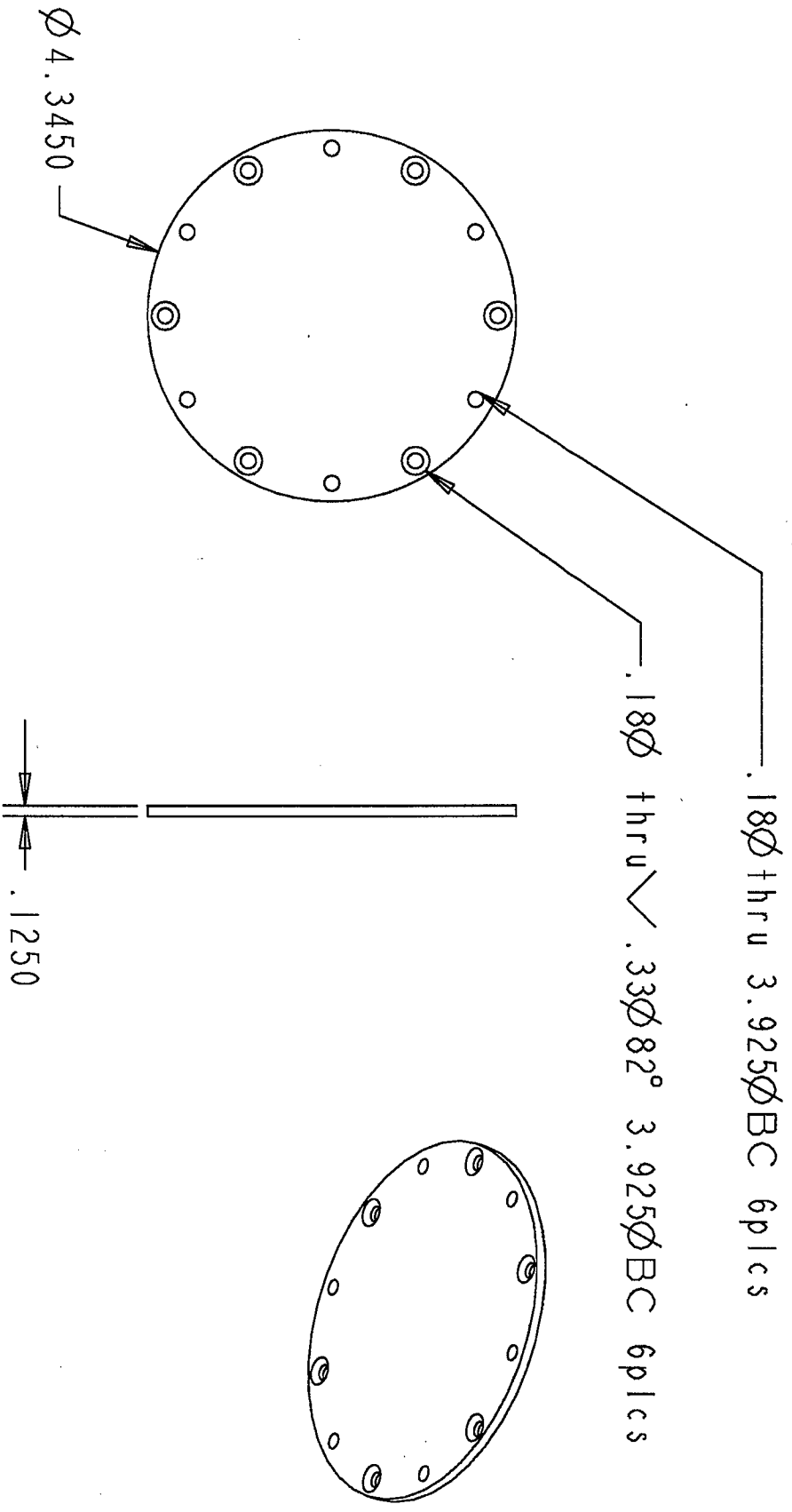
SECTION A-A

O RING GRVS
Ø LGE 3.650/3.660
WIDE .157/.163
T .101/.107
BOTH ENDS

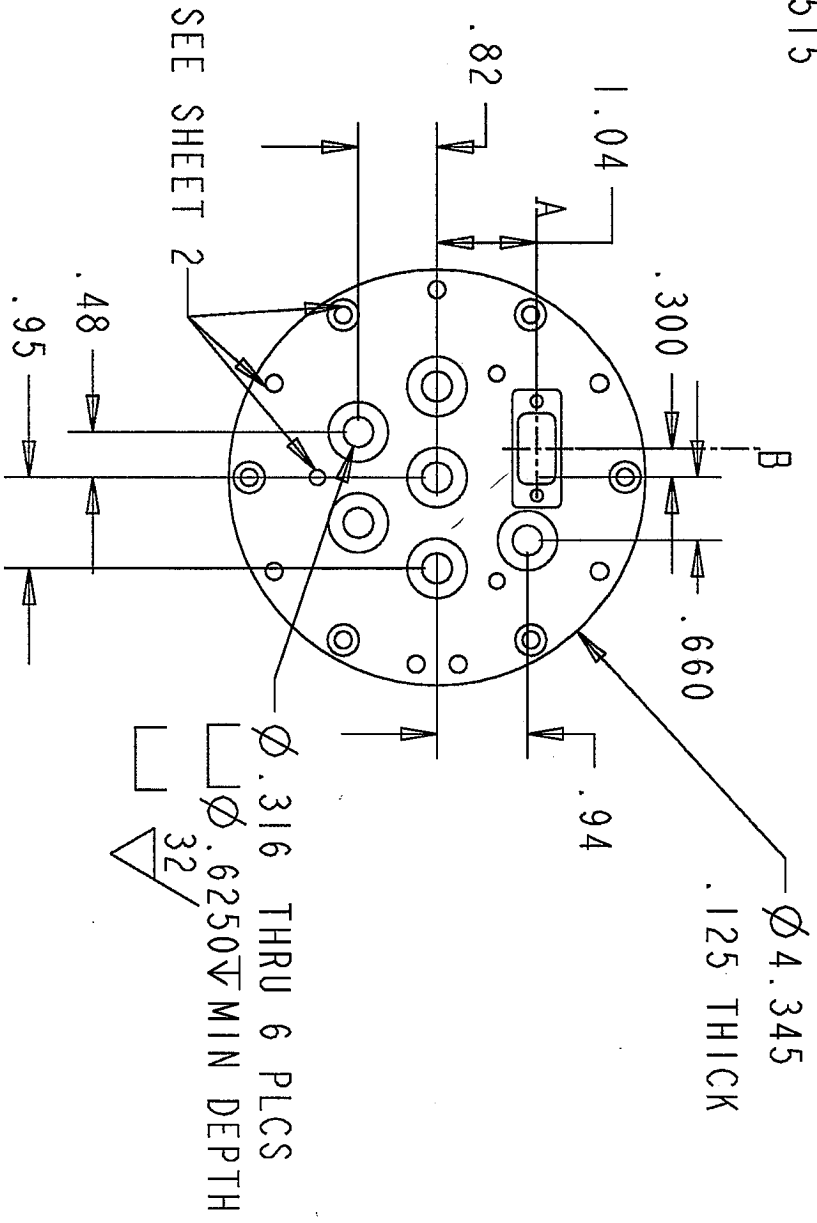
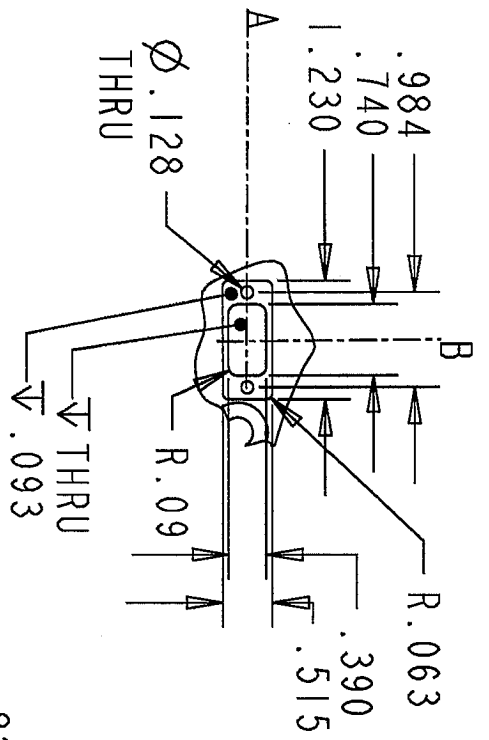


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Ø3.925 BC

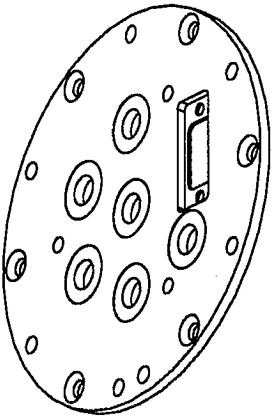
COMMENTS		TITLE	
NEXT ASSY ECD OVEN		ECD CAN	
MATERIAL 6061 AL		NITROUS OXIDE AND HALOCARBONS GROUP CLIMATE MONITORING AND DIAGNOSTICS LABORATORY NOAA/ERL	
FINISH ANODIZE BLK		SIZE A	DWG NO
		REV	



COMMENTS		TITLE	
NEXT ASSY ECD OVEN		NITROUS OXIDE AND HALOCARBONS GROUP CLIMATE MONITORING AND DIAGNOSTICS LABORATORY NOAA/ERL	
MATERIAL	SIZE	DWG. NO.	REV.
6061 AL	A		
FINISH BLK ANODIZE			



SEE SHEET 2



COMMENTS
NEXT ASSY
ADAPTOR SUB

TITLE
ECD TOP

NITROUS OXIDE AND HALOCARBONS GROUP
CLIMATE MONITORING AND DIAGNOSTICS LABORATORY
NOAA/ERL

MATERIAL
304 SS

SIZE
A

DWG NO

REV

Appendix C to NOAA/ESRL Safety Basis for Custom Radioactive ECD Ovens

MSDS for Nickel-63

Radioactive Material Safety Data Sheet

This data sheet presents information on radioisotopes only. This document is not subject to WHMIS requirements. For information on chemical compounds incorporating this radionuclide, see the relevant Material Safety Data Sheet.

Nickel-63

Part 1 – Radioactive Material Identification

Common Names: Nickel-63	Chemical Symbol: Ni-63 or ^{63}Ni
Atomic Number: 28	Mass Number: 63 (35 neutrons)
Chemical Form: Nickel metal	Physical Form: Nickel-63 is electroplated on one face of a thin nickel foil.

Part 2 – Radiation Characteristics

Physical half-life: 100.1 years **Specific Activity (GBq/g):** 2,190

Principle Emissions	E_{Max} (keV)	E_{eff} (keV)	Dose Rate (mSv/h/GBq at 1cm)	Shielding Required
Beta* (β)	65.9 (100%)	17	228 ^a	-
Gamma (γ) / X-Rays	-	-	-	-
Alpha (α)	-	-	-	-
Neutron (n)	-	-	-	-

* Where Beta radiation is present, Bremsstrahlung radiation will be produced. Shielding may be required.

Note: Only emissions with abundance greater than 10% are shown.

^a *The Health Physics and Radiological Health Handbook*, Scintra, Inc., Revised Edition, 1992

Progeny: Copper-63 (Cu-63)

Part 3 – Detection and Measurement

Methods of detection (in order of preference)

1. A radiation survey meter equipped with a thin-window, energy-compensated Geiger Mueller detector.
2. A radiation contamination monitor equipped with a Geiger Mueller pancake detector.
3. A radiation survey meter equipped with a plastic scintillator detector.

Dosimetry

Whole Body Skin Extremity Neutron

Internal:	Sealed sources pose no internal radiation hazard. However, in the event of loss of containment by the sealed source, all precautions should be taken to prevent inhalation or ingestion of the material.
Critical Organ(s):	not known at this time;
Annual dose limits:	<p><i>Non-nuclear energy workers:</i> 1mSv per year</p> <p><i>Nuclear energy workers:</i> a) 50 mSv in one year b) 100 mSv total over five years</p> <p><i>Pregnant nuclear energy workers:</i> 4 mSv over the balance of the pregnancy</p>

Part 4 – Preventive Measures

Always use the principles of time, distance and shielding to minimize dose

Engineering Controls:	Sealed radioactive sources used in industrial applications should always be within a protective source housing to minimize radiation dose and to protect the source capsule from damage.
Personal Protective Equipment	<i>(for normal handling of unsealed sources only. Always wear disposable gloves, safety glasses, personal protective equipment and clothing as appropriate to the material handled).</i> No special PPE required.
Special Storage Requirements:	None

Part 5 – Control Levels

Oral Ingestion	Inhalation	
ALI (kBq)	ALI (kBq)	DAC (Bq/ml)
333,000	74,000	2.59×10^{-2}
Exemption Quantity (EQ):	10,000,000	

Part 6 – Non-Radiological Hazards

<p>Identified as a potential carcinogen. In large doses, it has been known to cause cumulative lung damage and dermatitis.</p> <p><u>OSHA Permissible Exposure Limit (PEL)</u> 1 mg/m³ TWA</p>

Part 7 - Emergency Procedures

*The following is a guide for first responders. The following actions, including remediation, should be carried out by qualified individuals. In cases where life-threatening injury has resulted, **first** treat the injury, **second** deal with personal decontamination.*

Personal Decontamination Techniques

- Wash well with soap and water and monitor skin
- Do not abrade skin, only blot dry
- Decontamination of clothing and surfaces are covered under operating and emergency procedures

Spill and Leak Control

- Alert everyone in the area
- Confine the problem or emergency (includes the use of absorbent material)
- Clear area
- Summon Aid

Damage to Sealed Radioactive Source Holder

- Evacuate the immediate vicinity around the source holder
- Place a barrier at a safe distance from the source holder (min. 5 meters)
- Identify area as a radiation hazard
- Contact emergency number posted on local warning sign

Suggested Emergency Protective Equipment

- Gloves
- Footwear Covers
- Safety Glasses
- Outer layer or easily removed protective clothing (as situation requires)

This information was prepared by:

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Appendix D to NOAA/ESRL Safety Basis for Custom Radioactive ECD Ovens

Radiation Hazard of Agilent Technologies ECD Cell

SUBJECT: Radiation Hazard of Agilent Technologies ECD Cell

To Whom It May Concern:

Agilent Technologies, Inc. manufactures Electron Capture Detectors (ECDs). The ECD contains a 15 mCi source of radioactive Nickel-63. This source is enclosed within a steel housing. The device is listed as "**UN 2911 Radioactive material, excepted package, instruments**" for shipping purposes. A person receives a level of less than 0.00001% of the values listed below when the source is within an unopened detector housing.

Based upon an independent report¹, the level of radioactivity generated by the ⁶³Ni source in an unshielded condition (for example if the housing were to be opened or melted) is summarized below in regard to the risks to a human body:

SKIN DOSE: If the source were held in a hand, the thickness of skin on the hand would block all Beta Particles.

EYE DOSE: The thickness of the covering membrane on the eye will block all Beta Particles.

INHALATION DOSE: If vaporized, and all vapors were to be inhaled, the person would receive a dose of 93.75 rem. If a source were to be ground into 1 micrometer diameter particles and all particles were to be inhaled, the total body dose would be approximately 37.5 rem.

INGESTION DOSE: If the source were to be eaten, the person would receive a dose of 8.3 rem.

Persons working with an unshielded source at a distance of 16 cm from the source would require continuous exposure of 1,471 hours to obtain the annual public dose rate of 100 mrem. This assumes worst case conditions of exposure angle, source uniformity, and source radiation.

The charts on the following pages will provide better indications of the risk posed by the **UNSHIELDED ECD** ⁶³Ni source at a distance of 16 cm.

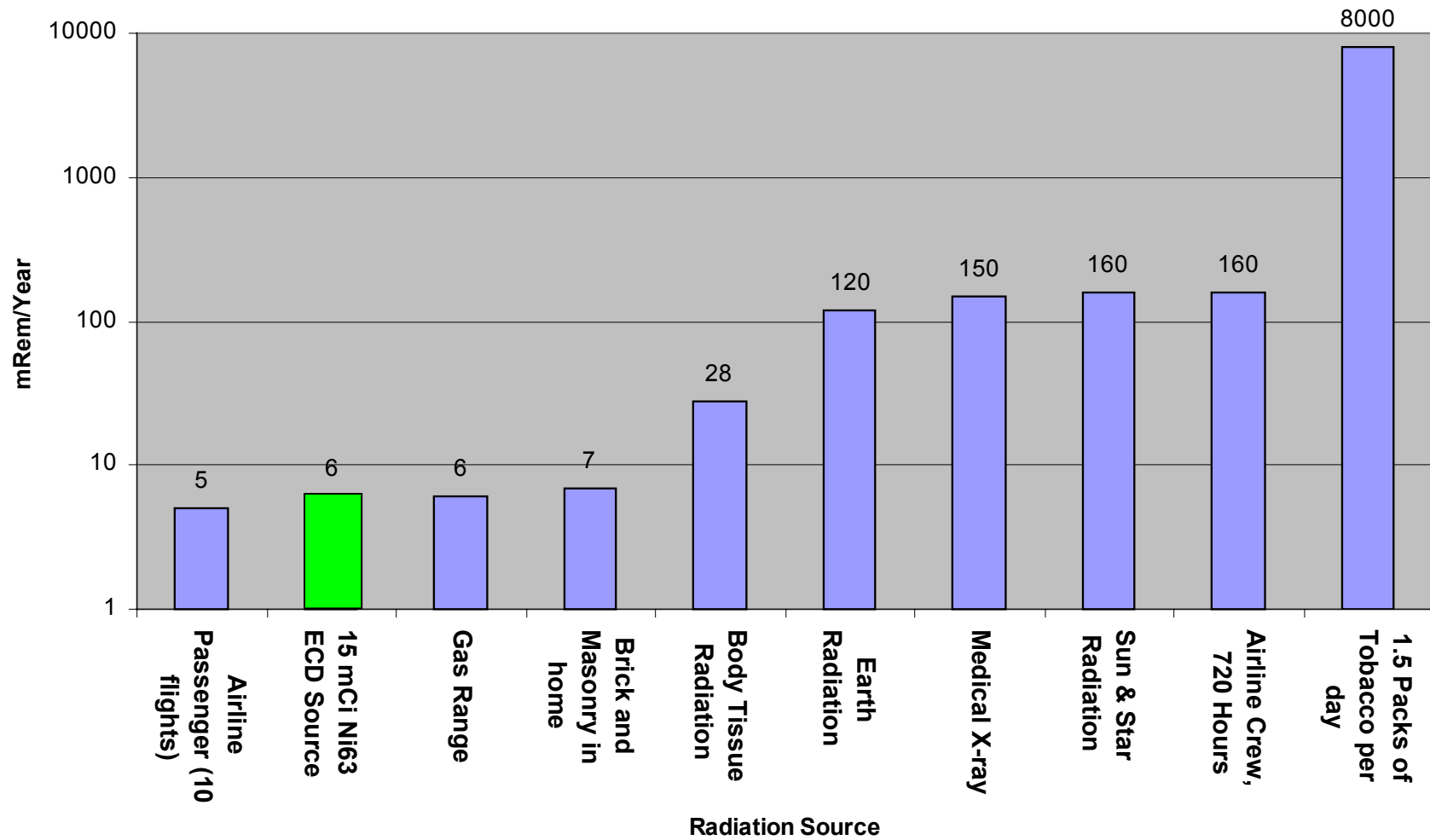
Sincerely,



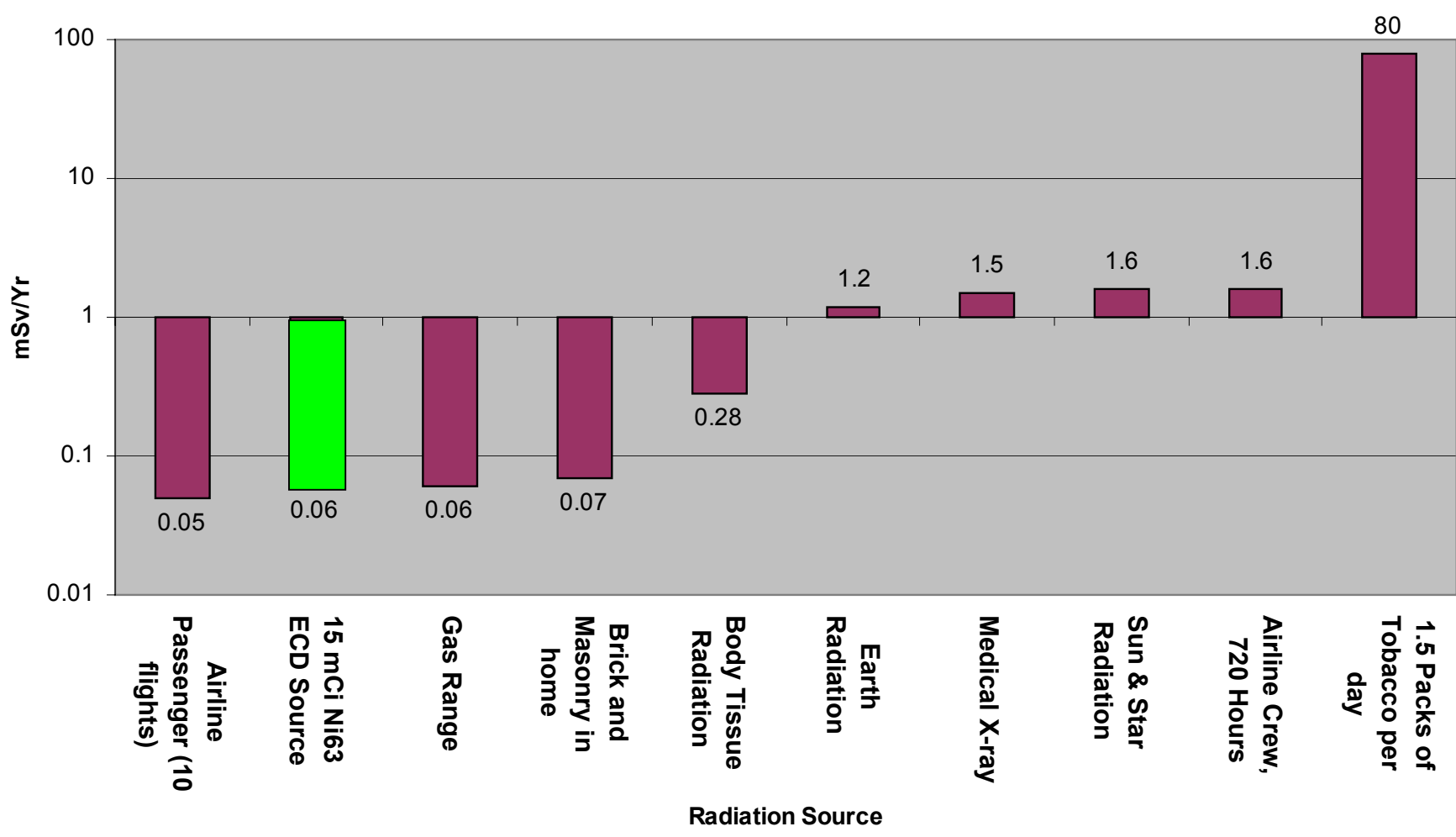
Wayne A. Hunter
Senior Engineer

¹ Report by Thomas E. Johnson, Ph.D., CHP and Alan Fellman, Ph.D., CHP: September 1999

Human Radiation Dosage per Year



Human Radiation Dosage per Year



Appendix E to NOAA/ESRL Safety Basis for Custom Radioactive ECD Ovens

49 CFR 173.424 Excepted packages for radioactive instruments and articles.

excepted packages prepared for shipment under the provisions of §173.421, §173.424, §173.426, or §173.428 must be certified as being acceptable for transportation by having a notice enclosed in or on the package, included with the packing list, or otherwise forwarded with the package. This notice must include the name of the consignor or consignee and one of the following statements, as appropriate:

(1) "This package conforms to the conditions and limitations specified in 49 CFR 173.421 for radioactive material, excepted package-limited quantity of material, UN2910";

(2) "This package conforms to the conditions and limitations specified in 49 CFR 173.424 for radioactive material, excepted package-instruments or articles, UN2910";

(3) "This package conforms to the conditions and limitations specified in 49 CFR 173.426 for radioactive material, excepted package-articles manufactured from natural or depleted uranium, or natural thorium, UN2910"; or

(4) "This package conforms to the conditions and limitations specified in 49 CFR 173.428 for radioactive material, excepted package-empty package, UN2910."

(b) An excepted package of Class 7 (radioactive) material that is classed as Class 7 and is prepared for shipment under the provisions of §173.421, §173.423, §173.424, §173.426, or §173.428 is not subject to the requirements of this subchapter, except for—

(1) Sections 171.15, 171.16, 174.750 and 176.710 of this subchapter, pertaining to the reporting of incidents and decontamination, when transported by a mode other than air;

(2) Sections 171.15, 171.16, and 175.700(b) of this subchapter pertaining to the reporting of incidents and decontamination when transported by aircraft; and

(3) The training requirements of subpart H of part 172 of this subchapter and, for materials that meet the definition of a hazardous substance or a hazardous waste, the shipping paper re-

quirements of subpart C of part 172 of this subchapter.

[Amdt. 173-244, 60 FR 50307, Sept. 28, 1995, as amended by Amdt. 173-244, 61 FR 20751, May 8, 1996; 62 FR 51561, Oct. 1, 1997; 63 FR 52849, Oct. 1, 1998]

§ 173.423 Requirements for multiple hazard limited quantity Class 7 (radioactive) materials.

(a) Except as provided in §173.4, when a limited quantity radioactive material meets the definition of another hazard class or division, it must be—

(1) Classed for the additional hazard;

(2) Packaged to conform with the requirements specified in §173.421(a)(1) through (a)(5) or §173.424(a) through (g), as appropriate; and

(3) Offered for transportation in accordance with the requirements applicable to the hazard for which it is classed.

(b) A limited quantity Class 7 (radioactive) material which is classed other than Class 7 in accordance with this subchapter is excepted from the requirements of §§173.422(a), 172.203(d), and 172.204(c)(4) of this subchapter if the entry "Limited quantity radioactive material" appears on the shipping paper in association with the basic description.

§ 173.424 Excepted packages for radioactive instruments and articles.

A radioactive instrument or article and its packaging is excepted from the specification packaging, shipping paper and certification, marking and labeling requirements of this subchapter and requirements of this subpart, if:

(a) Each package meets the general design requirements of §173.410;

(b) The activity of the instrument or article does not exceed the relevant limit listed in table 7 in §173.425;

(c) The total activity per package does not exceed the relevant limit listed in table 7 in §173.425;

(d) The radiation level at 10 cm (4 in) from any point on the external surface of any unpackaged instrument or article does not exceed 0.1 mSv/hour (10 mrem/hour);

(e) The radiation level at any point on the external surface of a package

§ 173.425

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bearing the article or instrument does not exceed 0.005 mSv/hour (0.5 mrem/hour), or, for exclusive use domestic shipments, 0.02 mSv (2 mrem/hour);

(f) The nonfixed (removable) radioactive surface contamination on the external surface of the package does not exceed the limits specified in § 173.443(a);

(g) Except as provided in § 173.426, the package does not contain more than 15 grams of uranium-235; and

(h) The package is otherwise prepared for shipment as specified in § 173.422.

§ 173.425 Table of activity limits—excepted quantities and articles.

The limits applicable to instruments, articles, and limited quantities subject to exceptions under §§ 173.421 and 173.424 are set forth in table 7 as follows:

TABLE 7—ACTIVITY LIMITS FOR LIMITED QUANTITIES, INSTRUMENTS, AND ARTICLES

Nature of contents	Instruments and articles		Limited quantity package limits ¹
	Limits for each instrument or article ¹	Package limits ¹	
Solids:			
Special form	10 ⁻² A ₁	A ₁	10 ⁻³ A ₁
Normal form	10 ⁻² A ₂	A ₂	10 ⁻³ A ₂
Liquids:			
Tritiated water:			
<0.0037 TBq/L (0.1 Ci/L)			37 TBq (1,000 Ci)
0.0037 TBq to 0.037 TBq/L (0.1 Ci to 1.0 Ci/L)			3.7 TBq (100 Ci)
>0.037 TBq/L (1.0 Ci/L)			0.037 TBq (1.0 Ci)
Other Liquids	10 ⁻³ A ₂	10 ⁻¹ A ₂	10 ⁻⁴ A ₂
Gases:			
Tritium ²	2 × 10 ⁻² A ₂	2 × 10 ⁻¹ A ₂	2 × 10 ⁻² A ₂
Special form	10 ⁻³ A ₁	10 ⁻² A ₁	10 ⁻³ A ₁
Normal form	10 ⁻³ A ₂	10 ⁻² A ₂	10 ⁻³ A ₂

¹ For mixtures of radionuclides see § 173.433(d).

² These values also apply to tritium in activated luminous paint and tritium adsorbed on solid carriers.

[Amdt. 173–244, 60 FR 50307, Sept. 28, 1995, as amended by Amdt. 173–244, 61 FR 20751, May 8, 1996; 63 FR 52849, Oct. 1, 1998; 65 FR 58630, Sept. 29, 2000; 66 FR 45383, Aug. 28, 2001]

§ 173.426 Excepted packages for articles containing natural uranium or thorium.

A manufactured article in which the sole Class 7 (radioactive) material content is natural or unirradiated depleted uranium or natural thorium and its packaging is excepted from the specification packaging, shipping paper and certification, marking, and labeling requirements of this subchapter and requirements of this subpart if:

(a) Each package meets the general design requirements of § 173.410;

(b) The outer surface of the uranium or thorium is enclosed in an inactive sheath made of metal or other durable protective material;

(c) The conditions specified in § 173.421(a) (2), (3) and (4) are met; and

(d) The article is otherwise prepared for shipment as specified in § 173.422.

[Amdt. 173–244, 60 FR 50307, Sept. 28, 1995, as amended by Amdt. 173–244, 61 FR 20752, May 8, 1996]

§ 173.427 Transport requirements for low specific activity (LSA) Class 7 (radioactive) materials and surface contaminated objects (SCO).

(a) In addition to other applicable requirements specified in this subchapter, low specific activity (LSA) materials and surface contaminated objects (SCO), unless excepted by paragraph (d) of this section, must be packaged in accordance with paragraph (b) or (c) of this section and must be transported in accordance with the following conditions:

(1) The external dose rate must not exceed an external radiation level of 10 mSv/h (1 rem/h) at 3 m from the unshielded material;

(2) The quantity of LSA and SCO material in any single conveyance must

Appendix F to NOAA/ESRL Safety Basis for Custom Radioactive ECD Ovens

49 CFR 173.421 additional requirements for excepted packages containing Class 7
(radioactive) materials.

§ 173.421

(1) Before initial filling and during periodic inspection and test, packagings must be cleaned in accordance with American National Standard N14.1.

(2) Packagings must be designed, fabricated, inspected, tested and marked in accordance with—

(i) American National Standard N14.1 (2001, 1995, 1990, 1987, 1982, 1971) (incorporated by reference, see §171.7 of this subchapter) in effect at the time the packaging was manufactured;

(ii) Specifications for Class DOT-106A multi-unit tank car tanks (§§179.300 and 179.301 of this subchapter); or

(iii) Section VIII, Division I of the ASME Code (incorporated by reference, see §171.7 of this subchapter), provided the packaging —

(A) Was manufactured on or before June 30, 1987;

(B) Conforms to the edition of the ASME Code in effect at the time the packaging was manufactured;

(C) Is used within its original design limitations; and

(D) Has shell and head thicknesses that have not decreased below the minimum value specified in the following table:

Packaging model	Minimum thickness; millimeters (inches)
1S, 2S	1.58 (0.062)
5A, 5B, 8A	3.17 (0.125)
12A, 12B	4.76 (0.187)
30B	7.93 (0.312)
48A, F, X, and Y	12.70 (0.500)
48T, O, OM, OM Allied, HX, H, AND G.	6.35 (0.250)

(3) Uranium hexafluoride must be in solid form.

(4) The volume of solid uranium hexafluoride, except solid depleted uranium hexafluoride, at 20 °C (68 °F) may not exceed 61% of the certified volumetric capacity of the packaging. The volume of solid depleted uranium hexafluoride at 20 °C (68 °F) may not exceed 62% of the certified volumetric capacity of the packaging.

(5) The pressure in the package at 20 °C (68 °F) must be less than 101.3 kPa (14.8 psia).

(b) Packagings for uranium hexafluoride must be periodically inspected, tested, marked and otherwise

conform with the latest incorporated edition of ANSI N14.1 (incorporated by reference, see §171.7 of this subchapter).

(c) Each repair to a packaging for uranium hexafluoride must be performed in accordance with the latest incorporated edition of ANSI N14.1 (incorporated by reference, see §171.7 of this subchapter).

[Amdt. 173-244, 60 FR 50307, Sept. 28, 1995, as amended at 67 FR 61014, Sept. 27, 2002]

§ 173.421 Excepted packages for limited quantities of Class 7 (radioactive) materials.

(a) A Class 7 (radioactive) material whose activity per package does not exceed the limits specified in §173.425 and its packaging are excepted from the specification packaging, marking, labeling and, if not a hazardous substance or hazardous waste, the shipping paper and certification requirements of this subchapter and requirements of this subpart if:

(1) Each package meets the general design requirements of §173.410;

(2) The radiation level at any point on the external surface of the package does not exceed 0.005 mSv/hour (0.5 mrem/ hour);

(3) The nonfixed (removable) radioactive surface contamination on the external surface of the package does not exceed the limits specified in §173.443(a);

(4) The outside of the inner packaging or, if there is no inner packaging, the outside of the packaging itself bears the marking “Radioactive”;

(5) Except as provided in §173.426, the package does not contain more than 15 grams of uranium-235; and

(6) The material is otherwise prepared for shipment as specified in accordance with §173.422.

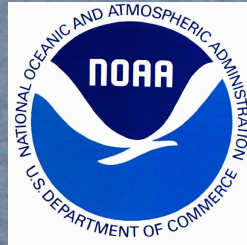
(b) A limited quantity of Class 7 (radioactive) material that is a hazardous substance or a hazardous waste, is not subject to the provisions in §172.203(d) or §172.204(c)(4) of this subchapter.

§ 173.422 Additional requirements for excepted packages containing Class 7 (radioactive) materials.

(a) Except for materials subject to the shipping paper requirements of subpart C of part 172 of this subchapter,

Appendix G to NOAA/ESRL Safety Basis for Custom Radioactive ECD Ovens

Powerpoint training for ECD safety.



Safety Of Radioactive Electron Capture Detectors (ECDs)

James W. Elkins, NOAA/ESRL

Contact information: 1 303 497 6224; E-mail:

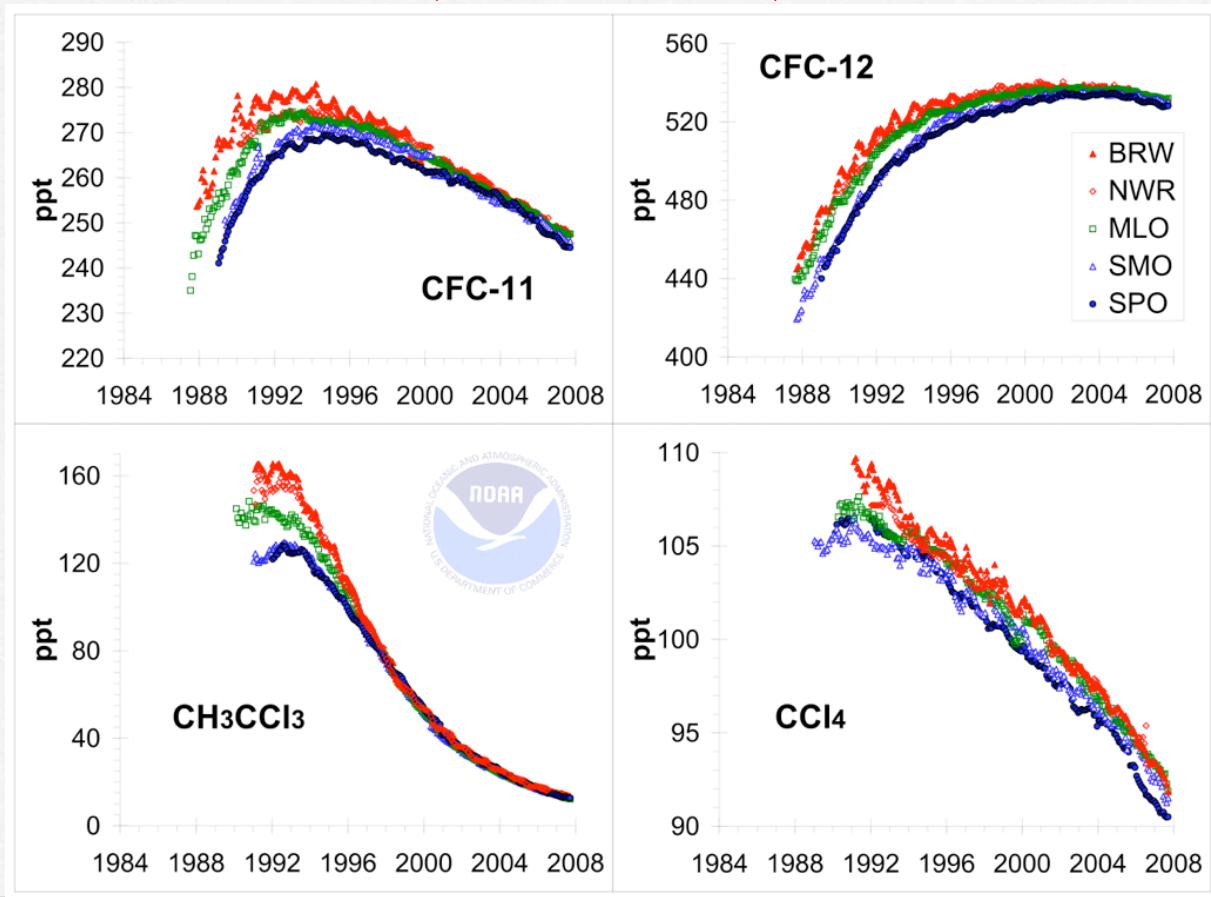
james.w.elkins@noaa.gov

Version 1.2, December 10, 2008



Why do we use ECDs?

Answer: NOAA has reporting responsibility to Congress for the U.S. Clean Air Act for compounds regulated by the Montreal Protocol (and it works).





Radiation 101

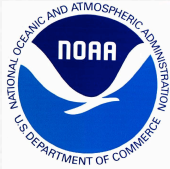


- Radioactive radiation is everywhere. Colorado has one of the highest backgrounds in the USA, >120 millirems per year (mrems/yr), because of our uranium mines, granite rocks, and high altitude enhancement of cosmic rays.
- We get an additional 40 mrems/yr from food and 200 mrems/yr from radon in air. Medical exposure is another 40-70 mrems/yr. *US average total yearly exposure is about 360 mrems/yr, but Colorado is 420 mrems/yr.* An opened 15 mCi ECD source yields 6 mrems/yr if you are 6 inches away from it. A sealed source yields μ mrems/yr.
- OSHA threshold = 100mrems/hr, serious blood problems occur >10,000 mrems/hr, with serious injury or death at >450000 mrems/hr.



Electron Capture Detectors (ECDs)

- Are in one the most commonly used analytical instrument, the Electron Capture Detector Gas Chromatograph (ECD-GC); NOAA/ESRL has over 140 ECDs.
- ECD uses Nickel-63 isotope on a platinum foil, emits high velocity electrons.
- Half Life of Nickel-63 = 92-101 years
- Radiation depends on manufacturer, 5-15 millicuries



Units of radioactivity: Source and Human Exposure Terms

- Source: $1 \text{ Ci} = 3.7 \times 10^{10} \text{ Bq}$ or electrons emitted per second.
- Smoke detector has a strength of 1 microcurie.
- ECDs (5-20 millicuries) are 5,000-20,000 times more radioactive than a smoke detector. But, it is sealed, but never open an ECD.
- Human exposure: 1 smoke detector exposure for a year is 0.008 mrems where rem = roentgen equivalent for man and roentgen = ergs (energy) of x-ray radiation per gram of tissue. ECDs are wiped tested for leaking radiation once every 6 months; if it passes the wipe test, the ECD has a leak of less < 0.005 microcurie. *So, 1 ECD exposure for a year is 200 times safer than the total source of a smoke detector.*



Major Types of radioactive radiation

- Alpha (fast moving Helium nucleus, 2 protons/ 2 neutrons), exposure can be serious because of mass (4 amu), stopped by single sheet of paper. Twenty times more dangerous for human exposure.
- Beta (fast moving electrons with 0 amu), **ECD radioactivity with 67 keV energy is converted into harmless thermal electron by 10-16 inches of air or one sheet of aluminum foil.**
- Gamma (high frequency radiation), X-rays, most serious, stopped by thick lead sheets.



How does the ECD work in a GC?

What is a Gas Chromatograph?

Separation and Detection (Electron Capture Detector, ECD) of Unknowns (one channel)

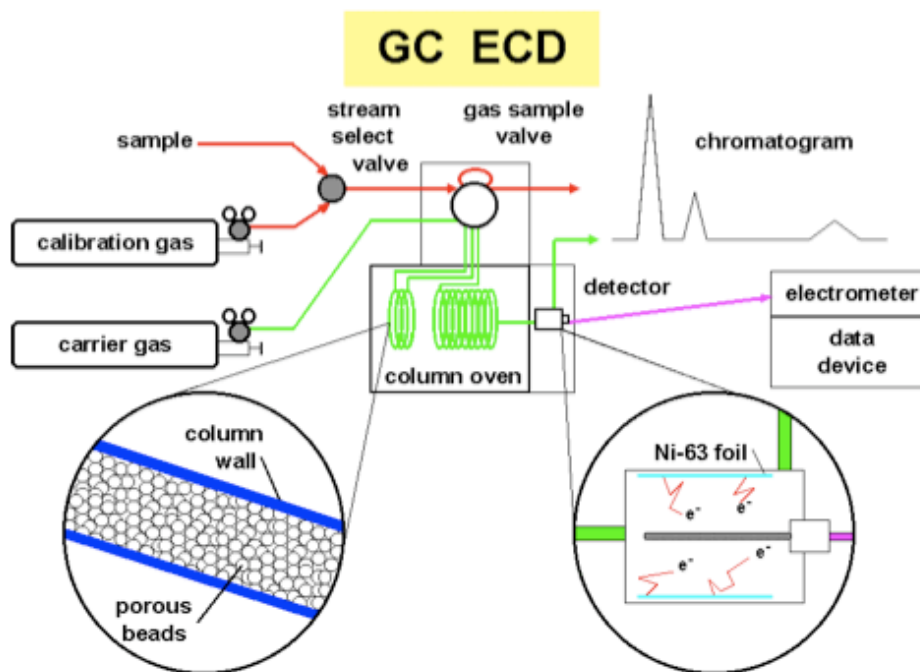


Diagram courtesy of Thayne Thompson

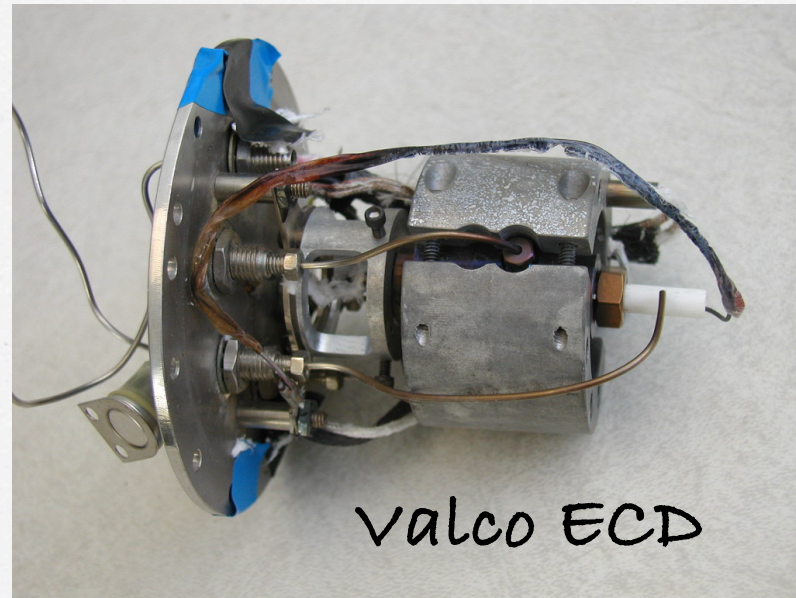


Typical ECD cells (~1" diameter, 1" long)

Shimadzu ECD



Valco ECD

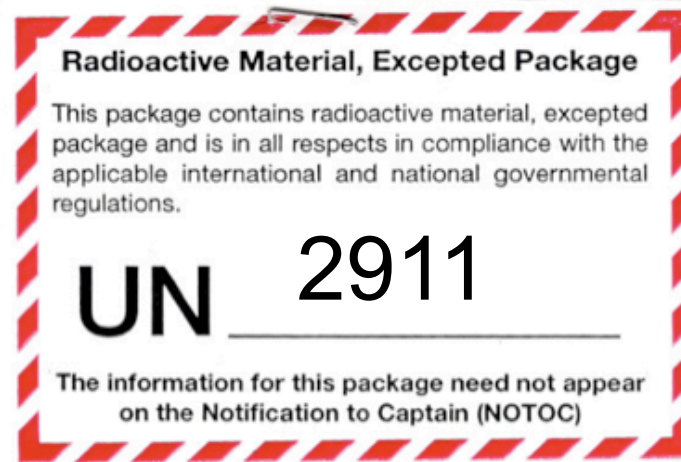


Station staff: *Wipe tests must be done every 6 months on working ECDs. Wipe tests are done before shipping and after shipment to final destination.* The test sheets should be wiped on the exhaust port on the outside of the can or ECD. Unused ECDs are stored in a locked cabinet in David Skaggs Research Center in Boulder, CO.



New Air Freight Shipping Labels Required for the Outside of the Box

New shipping labels for ECDs are required by US Department of Transportation (US DOT) and other international organizations. Use UN 2911 for ECDs. Contact Jim Elkins for stickers.





Summary

- ❑ *ECDs are sealed radioactive sources with little or no danger to you and the public. They are wipe tested for radioactivity twice a year, before shipment, and after arrival.*
- ❑ *If in doubt on any radioactive issue, contact your Radiation Safety Official (NOAA/Rhonda Carpenter, 303 497-3912).*
- ❑ *Never ever throw a radioactive source away in the trash, contact your RSO immediately for proper disposal.*
- ❑ *If an ECD cell is breached (smashed by heavy object), then don't touch it and tape off area. Call your RSO immediately. Never open the sealed source up, it is dangerous.*
- ❑ *New shipping label is required for air freight, contact the NOAA Certified Hazardous Material Traffic Manager (George Angel, 303 497-3670).*