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Nickel-Technetium Separation by Metal Distillation and Vapor Deposition PACRO Presentation

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To
Paducah Area Community Reuse Organization
(PACRO)
August 18, 2004

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Outline

- Introduction
- Physical Properties of Nickel & Technetium
- Ni-Tc Vapor Pressures
- Phase Diagrams of Ni/Tc System
- Mass Spectrometry
- Ni/Tc Batch Distillation & Vapor Deposition
- Conclusions

Introduction

- Gas diffusion Ni barriers used in U enrichment nuclear plants (Paducah, KY) are dismantled & melted.
- 9700 tons Ni volumetrically contaminated mainly with Tc and traces of U, Pu, Th, Np and other fission products.
- Tc amount has to be lowered to undetectable limits of radioactivity for release (>>1 Bq).
- Potential Markets: Scrap metal

Introduction Cont’d

- Methods of Separating Ni from Tc used:

  - Melt refining: surface contamination

  - Conventional Electrolysis: Tc co-deposits with Ni at cathode

  - Active Carbon columns (Wako Co. Ltd.): extracts Tc but not Ni, reduces conc. to 0.5% Tc

  - Teva Resin (Eichrom): $\alpha_{Tc/Ni} = 10^4$

  - Modified Electrolysis (British Nuclear Fuel): Cleaned Ni in Oak Ridge to 1Bq but was not released

- Institute of Physical Chemistry of the Russian Academy of Science collaborating with DOE:- Tc Reduction and sorption on sludge solids, Tc uptake by noble compounds & sodium aluminosilicates.

Introduction Cont'd

- Disadvantages of above processes:
  - Do not meet required release criteria
  - Large volumes of acid has to be used => generate waste => need treatment (Purex)
- We propose the physical vapor deposition of Ni: - T_b(Ni) > T_b(Tc)
  - P*(Ni) >> P*(Tc) => $\alpha_{Tc/Ni} > 10^6$
  - No generation of waste
  - Purification of Ni & Tc

Physical Properties

Carl Yaws, Chemical Properties Handbook, McGraw Hill, NY, 1999.

	M_w (g/mol)	T_m (K)	T_b (K)	T_c (K)	P_c (bar)	V_c (cm^3/mol)	ρ_c (g/cm^3)	Z_c	ω
Ni	58.69	1728	2415	6986.15	4918.5	35.4	1.6566	0.3	-0.17
Tc	99	2430	5000	17400.8	10183	42.6	2.2992	0.3	-0.31

	M_w (g/mol)	T_m (K)	T_b (K)	$\Delta H_f (T_m)$ (KJ/mol)	$\Delta H_v (T_b)$ (KJ/mol)
Ni	58.69	1728	2415	17.6	391.85
Tc	99	2430	5000	23.81	587.93

Ni-Tc Vapor Pressures

Carl Yaws, Chemical Properties Handbook, McGraw Hill, NY, 1999.

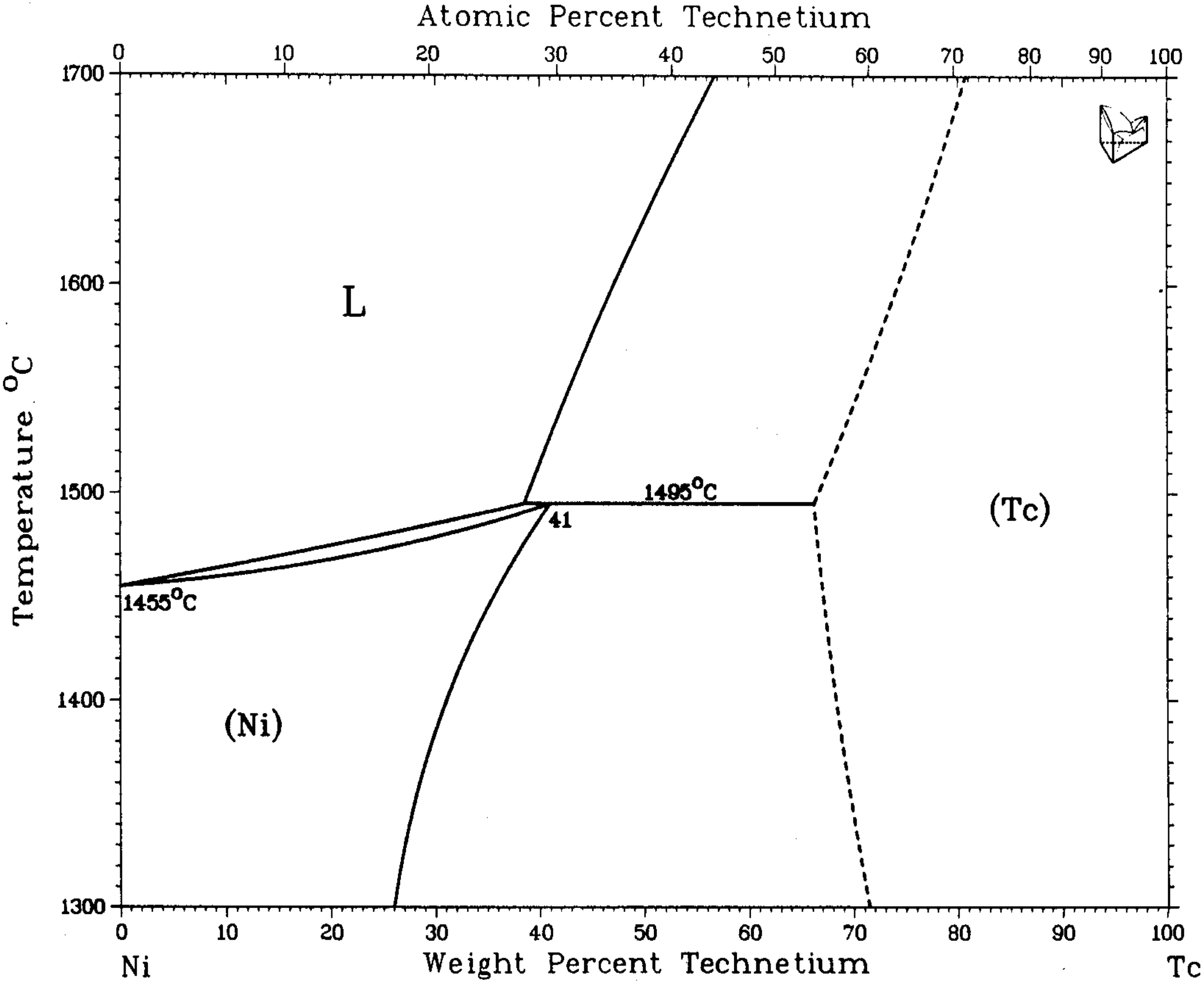
$\log(P^*) = A + B/T + C\log T + DT + ET^2$ P(mmHg) T(K)

	A	B	C	D	E	T range	T_m (K)	T_b (K)
Ni	-57.4301	-13533	23.611	-7.67E-03	7.81E-07	1061-2415	1728	2415
Tc	-240.5191	-5792.8	78.794	-1.31E-02	7.46E-07	1660-5000	2430	5000

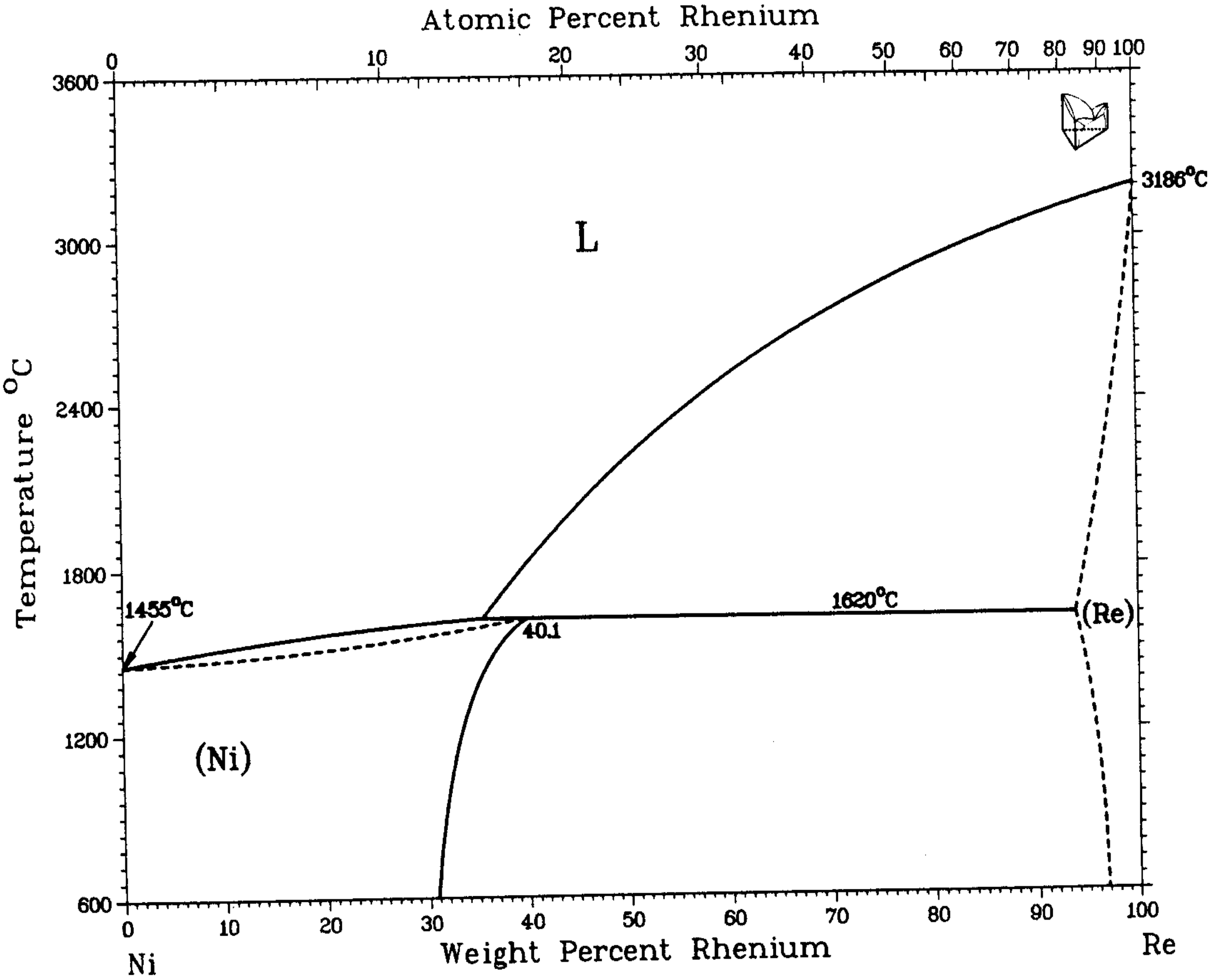
	P* (atm)		α
T (K)	Ni	Tc	
1200	1.09E-07	5.42E-21	2.02E+13
1500	8.23E-05	1.01E-15	8.11E+10
1728	2.42E-03	8.28E-13	2.92E+09
2415	1.00E+00	2.77E-07	3.61E+06
2430	1.00E+00	3.36E-07	2.97E+06

Phase Diagrams

- Ni-Tc phase diagram (P. Nash, The Ni-Tc (Nickel-Technetium) System, *Bulletin of Alloy Phase Diagram*, Vol 6, No. 2, 1985)
- Ni-Re phase diagram (A. Nash & P. Nash, The Ni-Re (Nickel-Rhenium) System, *Bulletin of Alloy Phase Diagram*, Vol 6, No. 4, 1985)
- Area of interest: >99% wt. Ni, T>1455^{o}C
- The phase diagrams illustrates that boiling of Ni from the mixture is possible. There are no formation of alloys.
- Initial experimentation: Ni-Re is nonradioactive & exhibits a similar phase diagram (peritectic) to Ni-Tc.


Atomic Percent Technetium
0
10
20
30
40
50
60
70
80
90
100
1700
1600
1500
1400
1300
Temperature °C
L
1495°C
41
1455°C
(Tc)
(Ni)
0
10
20
30
40
50
60
70
80
90
100
Ni
Weight Percent Technetium
Tc

P. Nash, 1985.



A. Nash and P. Nash, 1985

Mass Spectrometric Study

1) O.H. Krikorian, J.H. Carpenter, & R.S. Newbury, A Mass Spectrometric Study of the Enthalpy of Sublimation of Technetium. High Temperature Science, 1 (1969) 313-330.
2) Robert G. Behrens & Gary H. Rienhart, Vapor Pressure and Sublimation Enthalpy of Elemental Technetium. Journal of Less Common Metals, 75 (1980) 241-254.
3) Our Study

1) Krikorian et. al.

- Used a magnetic deflection mass spectrometer with a heater and an ionization source.
- Heating Element: Rhenium
- Mo is used as a standard
- Data Treatment:

- $P = N R T$ $N = G I F$ $I = \Sigma_j c_{m,j}$

- $F = (V_r m^{1/2} / \sigma B_m A t i_c) m/(\delta_{1/2})^2$

- $A = (1 / Z) \Sigma_i A_i Z_j$

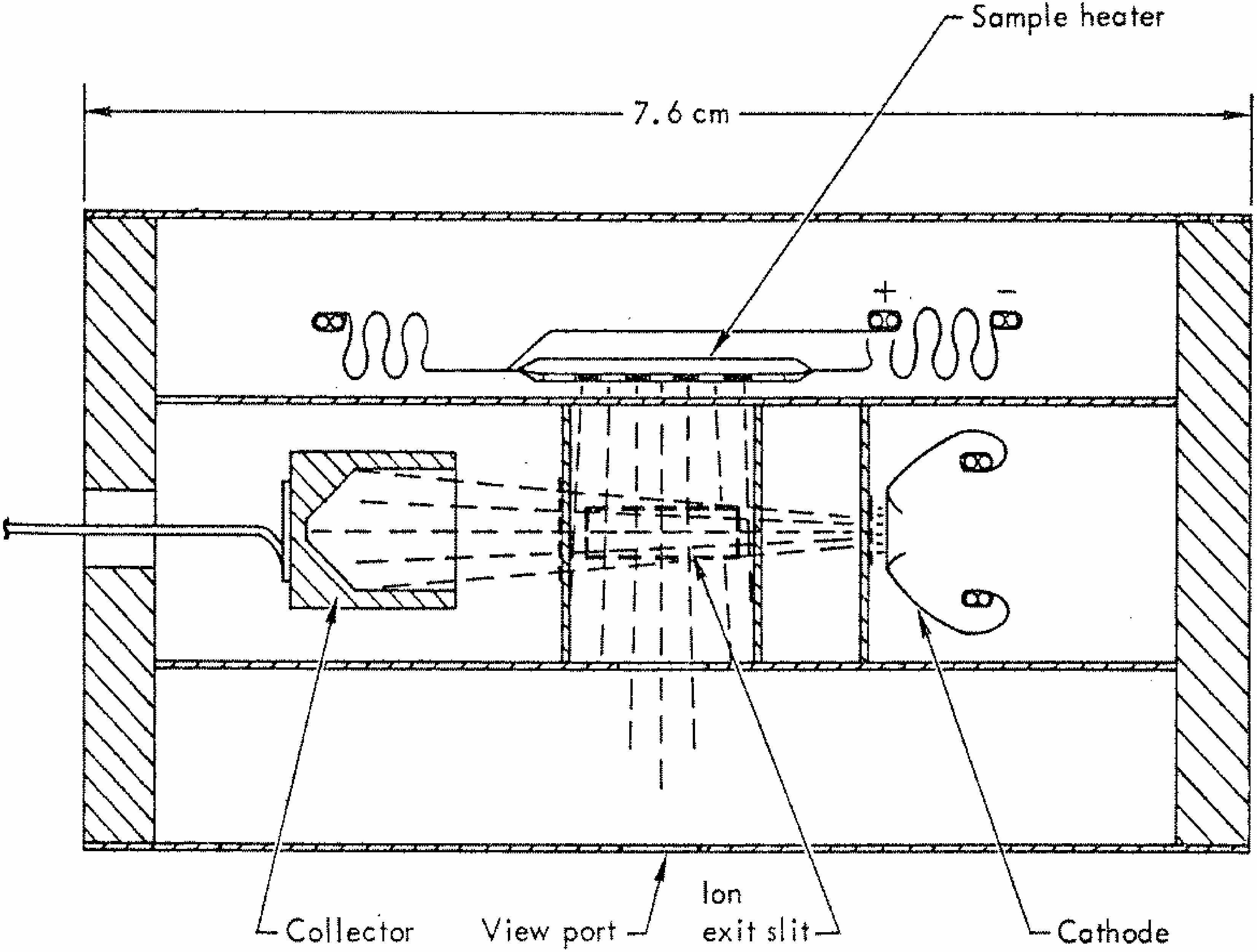


FIG. 2. Sample heater and ionization source.

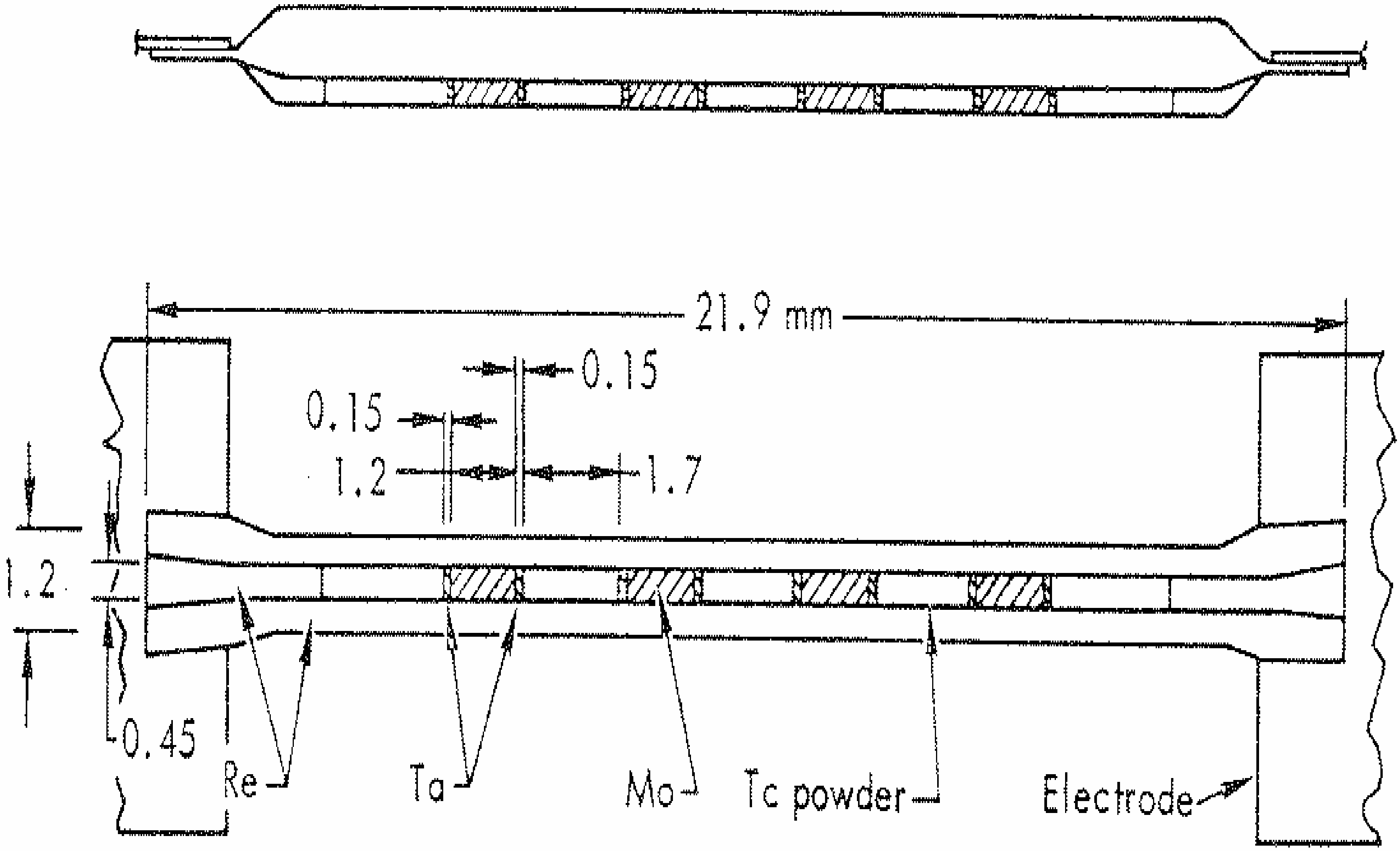


FIG. 3. Sample heater.

2) Behrens et. al.

- Used a Knudsen effusion cell mass spectrometer.
- Cell: Tantalum carbide
- Ag is used as a standard
- Data Treatment:

  - $P_{Tc} = C_s \, I_{Tc} \, T \, (f\sigma\gamma\tau) / (f\sigma\gamma\tau)_{Tc}$
  - $R \ln (P^*/P^o) = -\Delta H^o/T + \Delta S^o$

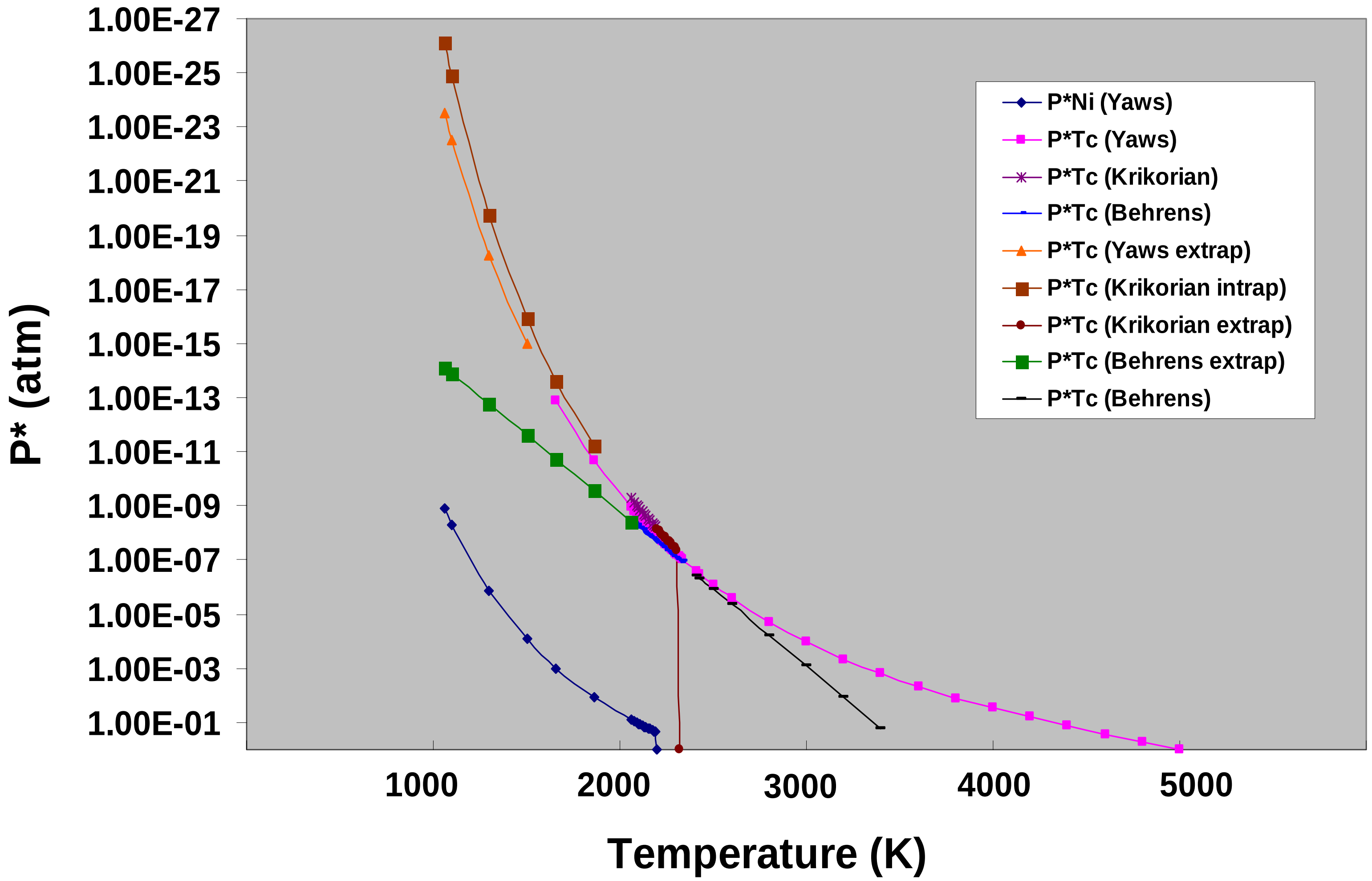
Comparison of Theoretical & Experimental Heats of Sublimation

$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$ within 10%error (Yaws)

Exp. Error = 0.8844 % (Krokorian et. al.)
1.17096 % (Behrens et. al.)

		ΔH_{sub} (KJ/mol)	higher limit	lower limit
Yaws	Ni	391.85	431.035	352.665
	Tc	587.93	646.723	529.137
Krikorian et. al.	Ni (exp)	418	421.69678	414.3032
	Tc (exp)	661.694	667.546	655.842
Behrens et. al	Tc (exp)	535.458	541.728	529.188

Comparison of Vapor Pressures of Tc



Our Study

- Knudsen Effusion Cell coupled to a Quadrupole Mass Spectrometer
- Cell: Tungsten
- Standard: pure Ni
- Use Data treatment:

- $P_i = K\ I_i\ T / \sigma_i$

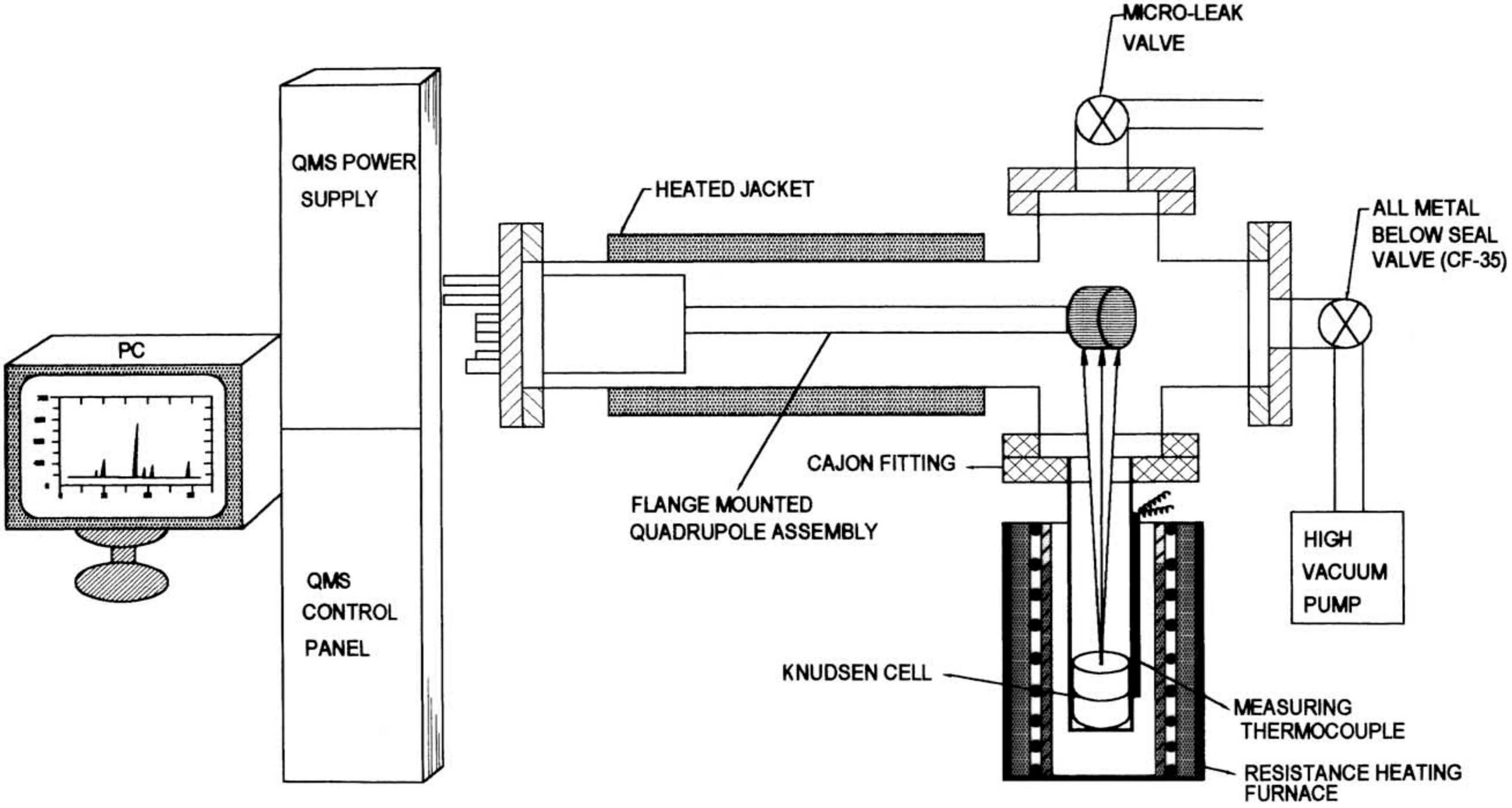
- $R \ln (P^*/P^o) = -\Delta H^o/T + \Delta S^o$

- $\ln (P^*) = \ln(I\ T) + \ln K + \ln \sigma_i$

- $R \ln (I\ T) = -\Delta H^*/T + c$

- $\Delta H^* - \Delta H^o$ = enthalpy barrier for the kinetically slow steps of the vaporization process

Knudsen Effusion Cell Mass Spectrometer



Batch Distillation of Ni/Tc

- 1) 9700 tons of Ni contaminated with Tc
- 2) 10 batches for 1year
- 3) Ni/Tc feed: 30.76g/s with 4148 ppb Tc
- 4) T = 2430K
- 5) $\alpha_{Ni/Tc} = 2.97\mathrm{x}10^6$
- 6) $(n_{Ni} / n_{Ni}{}^o = (n_{Tc} / n_{Tc}{}^o)^\alpha$
- 7) $\alpha_{Ni/Tc} = P^*_{Ni}/P^*_{Tc} = (V_{Ni} / V_{Tc})/(n_{Ni} / n_{Tc})$
- 8) Ni vapor is deposited on a cold surface & deposited to make thin sheets.

Calculation

n_{Tc} (kmol/s)	n_{Ni} (kmol/s)	V_{Tc} (kmol/s)	V_{Ni} (kmol/s)	V'_{Tc} (kg/s)	V'_{Ni} (kg/s)	S_{Ni} (kg)	Day
4.06E-02	16527.45	4.34E-16	5.24E-04	4.E-14	0.0308	2658	1
4.06E-02	15169.03	4.73E-16	5.24E-04	5.E-14	0.0308	79726	30
4.06E-02	13810.61	5.20E-16	5.24E-04	5.E-14	0.0308	159451	60
4.06E-02	11999.38	5.98E-16	5.24E-04	6.E-14	0.0308	265752	100
4.06E-02	7471.31	9.60E-16	5.24E-04	1.E-13	0.0308	531505	200
4.06E-02	2943.24	2.44E-15	5.24E-04	2.E-13	0.0308	797257	300
4.06E-02	2037.63	3.52E-15	5.24E-04	3.E-13	0.0308	850407	320
4.06E-02	1132.02	6.34E-15	5.24E-04	6.E-13	0.0308	903558	340
4.06E-02	679.21	1.06E-14	5.24E-04	1.E-12	0.0308	930133	350
4.06E-02	452.81	1.58E-14	5.24E-04	2.E-12	0.0308	943421	355
4.06E-02	181.12	3.96E-14	5.24E-04	4.E-12	0.0308	959366	361
4.06E-02	135.84	5.28E-14	5.24E-04	5.E-12	0.0308	962023	362
4.06E-02	90.56	7.92E-14	5.24E-04	8.E-12	0.0308	964681	363
4.06E-02	45.28	1.58E-13	5.24E-04	2.E-11	0.0308	967338	364
4.06E-02	1.00E-07	7.18E-05	5.24E-04	7.E-03	0.0308	969996	365

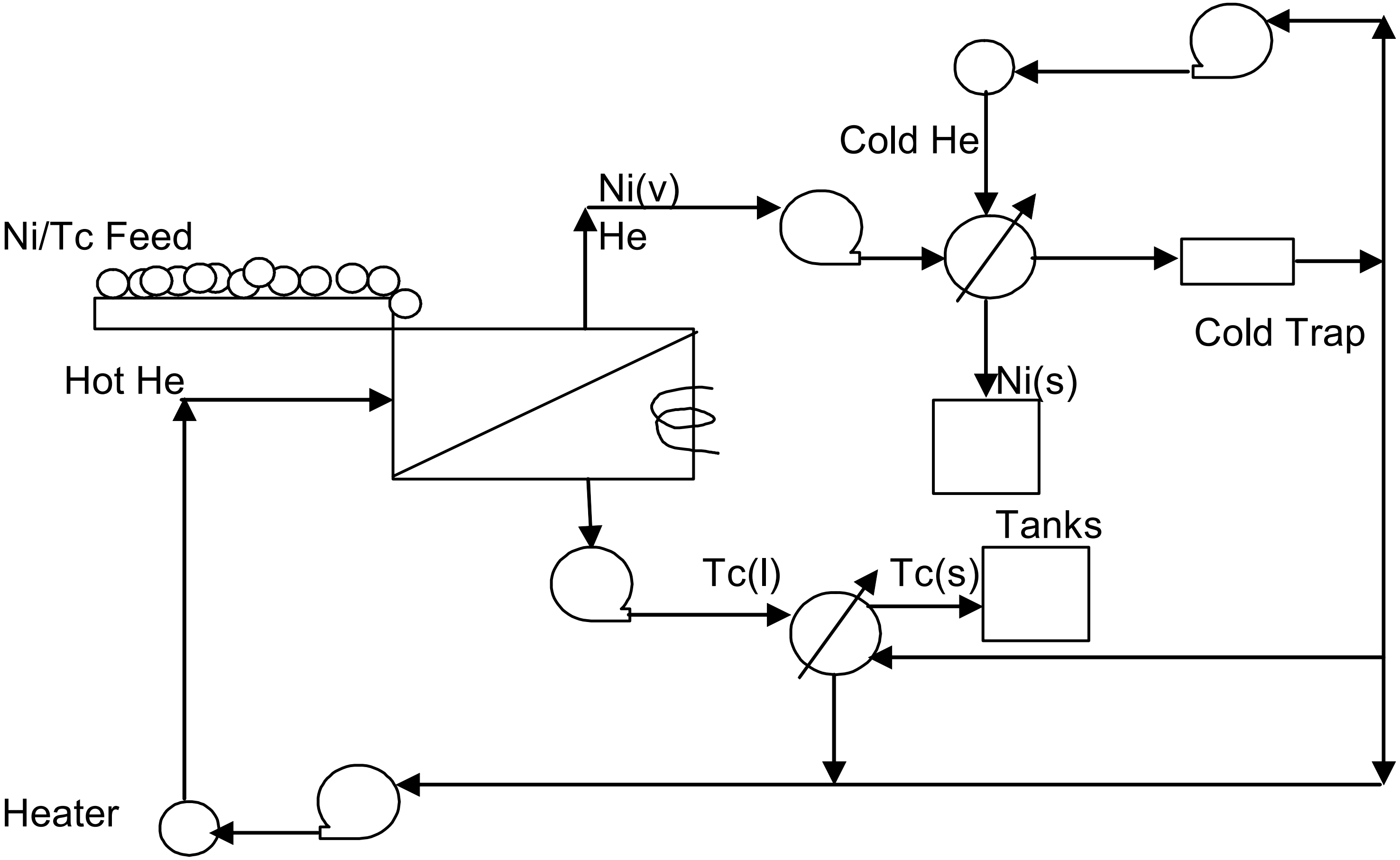
Calculation Cont’d

x_{Tc}	x_{Ni}	y_{Tc}	y_{Ni}	y'_{Tc}	y'_{Ni}	Day
2.4591E-06	0.999998	8.28E-13	1	1.40E-12	1	1
2.68E-06	0.999997	9.03E-13	1	1.52E-12	1	30
2.94E-06	0.999997	9.91E-13	1	1.67E-12	1	60
3.39E-06	0.999997	1.14E-12	1	1.92E-12	1	100
5.44E-06	0.999995	1.83E-12	1	3.09E-12	1	200
1.38E-05	1.00E+00	4.65E-12	1	7.85E-12	1	300
1.99E-05	1.00E+00	6.72E-12	1	1.13E-11	1	320
3.59E-05	1.00E+00	1.21E-11	1	2.04E-11	1	340
5.98E-05	1.00E+00	2.02E-11	1	3.40E-11	1	350
8.98E-05	1.00E+00	3.02E-11	1	5.10E-11	1	355
2.24E-04	1.00E+00	7.56E-11	1	1.28E-10	1	361
2.99E-04	1.00E+00	1.01E-10	1	1.70E-10	1	362
4.49E-04	1.00E+00	1.51E-10	1	2.55E-10	1	363
8.97E-04	9.99E-01	3.02E-10	1	5.10E-10	1	364
1.00E+00	2.46E-06	1.20E-01	1	1.88E-01	1	365

Calculation Cont’d

Tc	**Activity**	**Recovery**	**Day**
ppbm	**Bq**	**of Ni (%)**	
1.40E-03	2.70E-02	0.27	1
1.52E-03	2.94E-02	8.22	30
1.67E-03	3.23E-02	16.44	60
1.92E-03	3.71E-02	27.40	100
3.09E-03	5.96E-02	54.79	200
7.85E-03	1.51E-01	82.19	300
1.13E-02	2.19E-01	87.67	320
2.04E-02	3.93E-01	93.15	340
3.40E-02	6.56E-01	95.89	350
5.10E-02	9.84E-01	97.26	355
1.28E-01	2.46E+00	98.90	361
1.70E-01	3.28E+00	99.18	362
2.55E-01	4.92E+00	99.45	363
5.10E-01	9.84E+00	99.73	364
1.88E+08	4.45E+09	100.00	365

Ni/Tc Separation Plant



Decontamination 9700 tons of Nickel

	Price($)/kg	mass (kg)	Price ($) for 90% Rec
Ni Price/Kg	6.952	9,699,960	60,690,708
Tc Price/Kg	50,000	40	1,810,602
Ni / Tc		9700000	62,501,310

	Cost($)/kg	Cost($)/Prod	Profit	Savings *	Savings **
Electrolysis					
Ni (1 Bq)	**5.61**	**54,417,000**	**6,273,708**	**40,844,508**	**46,315,308**
Sold Ni & Tc			**8,084,310**	**42,655,110**	**48,125,910**
Nevada (disposal)	3.564	34,570,800			
Envirocare	4.128	40,041,600			
Our Process					
Ni (0.027-0.3 Bq)	**1.14**	**11,021,260**	**49,669,448**	**84,240,248**	**89,711,048**
Sold Ni & Tc			**51,480,050**	**86,050,850**	**91,521,650**

* Disposal at Nevada
** Disposal at Envirocare

Conclusions

- The vaporization of Ni could be used to separate Ni from Tc due to high differences in boiling points and relative volatility.
- Mass Spectrometry is an efficient method to determine concentrations, vapor pressures, and enthalpies of Ni/Tc system.
- Batch distillation achieves higher purities of Ni & lower costs than electrorefining & electrolysis methods.

Evolution of Environmental Issues

Treatment → Sustainable Science and Engineering

End-of-Pipe Treatment

- reactive
- Reliance on abatement
- Regulation driven
- No regard for resource consumption
- Low accountability

Pollution Prevention

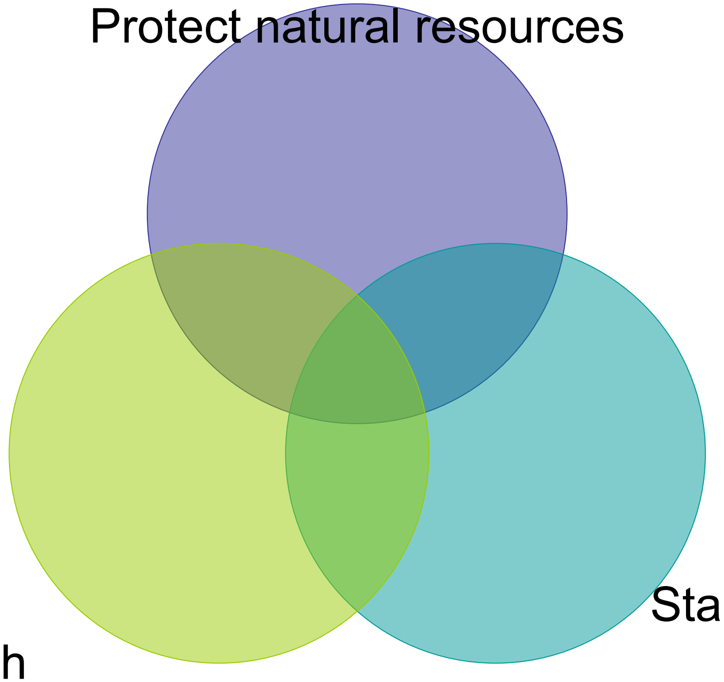
- Reduce
- Reuse
- Recycle

Design for environment

- Proactive
- Beyond compliance
- Life cycle analysis
- ISO 14000
- Extended product responsibility
- Benchmarking

Sustainable development

- Triple bottom line: economic, environmental, social
- Multifaceted accountability for public, private sectors



Environmental:
Human health
Ecosystem health
Biodiversity
Protect natural resources

Economic:
Productivity
Technological growth
Profit and employment

Societal:
Informed citizens
Stakeholder participation
Social justice
Equal opportunity
Wealth distribution