TRACE ANALYSIS AND ULTRAPURIFICATION OF MATERIALS FOR OPTICAL WAVEGUIDE TECHNOLOGY

James W. Mitchell

Bell Laboratories, Murray Hill, New Jersey 07974, USA

Abstract - In the telecommunications industry techniques for purifying and characterizing materials, and analytical methods for solving chemical problems have been vitally important for technological progress. The application of reliable analytical methods to determine optimum conditions for preparing materials in controlled states of purity continues to be essential. In fact, the production of materials with unique properties, determined by doping precisely with impurities on the one hand or by insuring the absence of other detrimental ones, continues to be a key to technological advancement.

The most recent critical need in the industry for pure materials and ultratrace analysis resulted from the initiation of applied research and development of optical waveguide systems, where tolerance limits for waveguide materials were projected to be in the 2 to 100 ng/g range for commonly found transition metal impurities Fe, Co, Cr, Cu, Mn, Ni, and V. Applications of neutron activation, X-ray fluorescence, atomic absorption,and laser intracavity absorption spectroscopy in support of optical waveguide programs will be discussed. Examples will be provided to demonstrate the use of these techniques for screening commercially available glass-making raw materials and chemical vapor deposition reagents, for unequivocally identifying impurities in glasses and fibers, and for detecting sources of contamination during glass-making and fiberdrawing.

In the absence of materials of sufficient purity from available commercial sources, specialized preparations have been performed under controlled executions of solvent extraction, ion exchange, mercury cathode electrolysis, and low temperature sublimation. The advantages and pitfalls of these methods will be compared. It will be demonstrated that radioisotope techniques and activation analysis are the most powerful and reliable tools for establishing optimum conditions for executing these procedures and for pinpointing specific deficiencies of each purification process. Factors limiting the ultimate state of purity achievable for analytical reagents for trace analysis will be discussed.

INTRODUCTION

Many industries in the United States are quite dependent upon analytical chemistry for their growth and ultimate success. The communication industry provides a particular example where techniques for purifying and characterizing materials, and methods for solving chemical problems have been vitally important for technological advancements. As is now well recognized the first real revolution in communication technology followed the development of zone refining techniques at Bell Laboratories. This process made it possible to prepare extremely pure silicon, germanium, and other materials from which semiconductor devices could be processed. Soon after this discovery materials were fabricated with such high degrees of purity that trace elements could not be easily detected by existing analytical methods. Thus electrical tests, such as resistivity and others were used. Although these electrical methods were very useful, they were nonspecific; and it was not

possible to identify the impurities present. As a result, analytical research
to develop extremely sensitive, specific methods was stimulated and has con-
tinued to be a primary factor essential in technological research and devel-
opment.

As is already evident instrumental and chemical methods for trace analysis
have been developed and applied to a wide variety of materials character-
ization problems. Many materials in controlled states of purity are required
for fabricating various components of telecommunications systems. In fact
the production of materials with important properties has been one of the
keys to technological advancement in the communications industry. A few
examples of materials and important properties are listed in Table 1.

TABLE 1. Materials required in controlled states of purity

Material	Application	Controlled Impurities
Silicon	Device production	Defects, Na, B, P, Cl, As, O, Al
Germanium	Radiation detectors	
Fused silica	Containers, fiber optic cladding	Transition elements (Tr,M's)
MCVD preforms	Optical fibers	Fe, Cu, Ni, Cr, Mn, Co, -OH
GaP, GaAs	LED's , Lasers	O, C, N, Cl, P, other Tr.M's
Quartz	Piezoelectric resonators	Fe, Al, -OH
Platinum	Containers	Fe, Ir
Gold	Plating	Fe, Sn, Pb, C
Cu-Ni-Sn	Spring alloys	P, Pb, Ti, Si, Y
Graphite	Varister manufacture	Al, Fe
Silicon carbide		

The properties of some materials change dramatically with impurity content
and with variation in composition. Low ppb levels of certain impurities in
semiconductors and glass will render the material completely useless for the
intended application while certain properties are only obtained by precisely
doping materials with known amounts of important trace elements.

The most recent critical need in the telecommunications industry for pure
materials and trace element analyses occurred with the initiation of research
to develop optical waveguide systems. Although today's telephone systems
depend largely on transmission of electrical signals via copper conductor
cables, systems of the future will be based on combinations of electrical and
optical transmission components. A schematic diagram of a representative
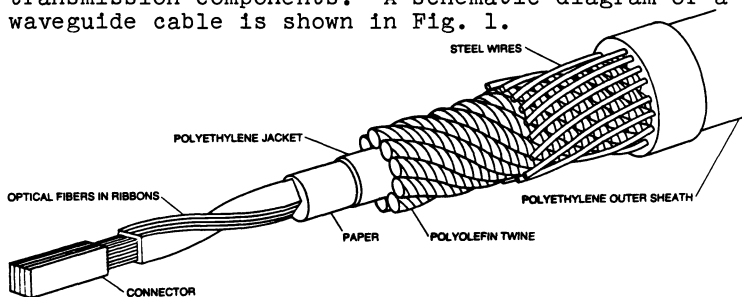optical waveguide cable is shown in Fig. 1.

Fig. 1. Optical waveguide cable system

An optical waveguide is essentially a light pipe into which light of appropriate characteristics is launched from a suitable LED or laser source and then is propagated through the fiber via total internal reflection from the core-cladding interface. Because the transmission bandwidth capacity of the fiber is extremely large and its physical dimensions exceedingly small in comparison to other systems in use today, the worldwide telecommunications industry is very active in applied research, development and deployment of optical waveguide systems.

Glass has emerged as the most suitable material for fabricating optical waveguides. To be useful for this purpose the material must be devoid of impurities that would attenuate the propagating light via absorption losses. Projected tolerance limits for certain transition elements in glasses of various composition are given in Table 2.

TABLE 2.   Impurity levels (PPB) introducing 1 dB/Km absorption
           losses at 800 nm in various glasses

Impurity	Na-Ca-Si	SiO_2	Na-B-Si
Co	0.2	40	100
Cr	2.1	2	20
Cu	5.1	100	1(II)*, 10(I)*
Fe	2.1	20	1(II)*, 1000(III)*
Mn	10.1	50	100
Ni	2.1	40	10
V	10.1	1	25

* (I), (II), (III) are oxidation states of impurities

SCOPE AND OBJECTIVES OF ANALYTICAL PROGRAM

The analytical information required for supporting the waveguide research program included, rapid screening of available glasses and glassmaking raw materials to determine their suitability for waveguide production, identifying impurities present in these materials, detecting sources of contamination during glassmaking and fiber drawing, and developing procedures for preparing materials of sufficient purity in the event commercially available products were too impure. To obtain this information extremely sensitive and reliable quantitative methods were required since small changes in the levels of various traces would need to be distinguished. The appropriate support method could be chosen from the listing of analytical techniques in Table 3. Neutron activation analysis (NAA) was selected as the primary support method because of its characteristic features of [1] sufficient sensitivity for direct sub-ppm and sub-ppb detection of a large number of trace elements, [2] application for rapid, semi-quantitative survey determinations of a large number of elements or highly accurate, selective, single element determinations using chemical separations, and [3] freedom from blank problems that could occur during post-irradiation chemical processing of the sample. X-ray fluorescence (XRF), atomic absorption spectroscopy (AAS), and laser intra-cavity absorption spectrophotometry have also been applied.

TABLE 3.   Techniques for trace and ultratrace analysis

Atomic absorption spectroscopy (AAS)

Atomic fluorescence spectroscopy(AFS)

Coulometric titration

Electron-capture gas-liquid chromatography

Electronprobe microanalysis

Emission spectroscopy (ES)

Fluorimetry

Ion-specific electrodes

Kinetic measurements

Mass spectroscopy (MS)

Neutron activation (NAA)

Nuclear track counting

Polarography

Radioisotope dilution (RID)

RF induction coupled atomic emission

Stable isotope dilution (SID)

Spectrophotometry

Titrimetric methods

X-ray fluorescence (XRF)

SURVEYS OF THE PURITY OF COMMERCIALLY AVAILABLE MATERIALS

Neutron activation with gamma-ray spectroscopy was used to screen commercial samples of sodium and calcium carbonate to detect Fe, Cr, and Co impurities. Inspection of gamma-ray spectra is used to select the most pure compound in a series of samples irradiated simultaneously. Sample A in Fig. 2 is clearly the most pure product with respect to impurities of interest.
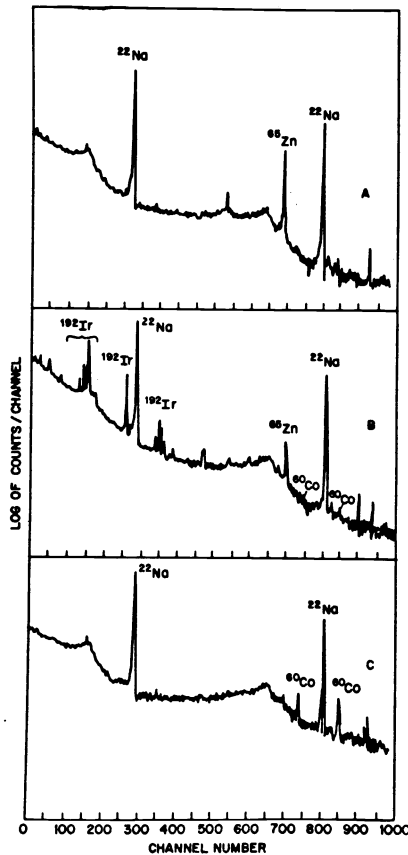

Fig. 2. Gamma-ray spectra of sodium carbonates.

Spectra of $CaCO_3$ samples distributed by suppliers of lightguide materials are shown in Fig. 3. Characteristic photopeaks, for ^{60}Co, ^{51}Cr, and ^{46}Sc are present in Sample B.
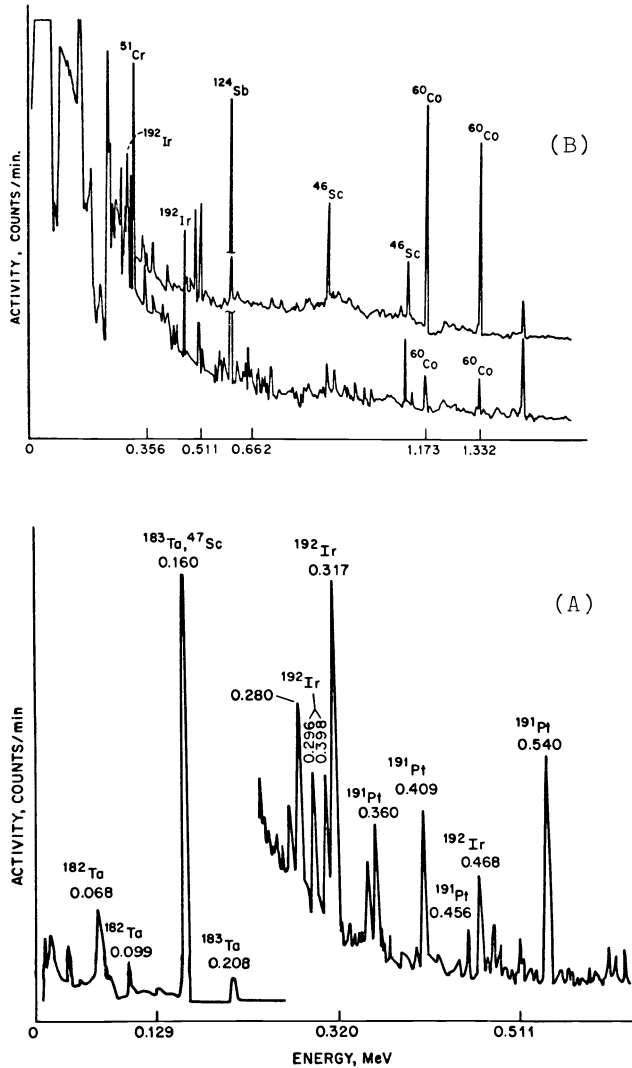

Fig. 3.   Gamma-ray spectra of calcium carbonate.

Additional impurities in Sample A include full energy peaks for ^{182}Ta, ^{183}Ta, ^{192}Ir, ^{191}Pt, and ^{195m}Pt. The detection of ^{191}Pt ($T_{1/2}$ = 3.00d) after a 13d decay period showed considerable contamination by this rare trace element. This was subsequently related to the use of platinum containers for thermal decomposition of a high-purity precursor compound to obtain calcium carbonate. Iridium, an additive of platinum to increase hardness, is detected with very high sensitivity. Because of its large cross section and long half-life, detection of this isotope serves as a sensitive probe to determine contamination from platinum containers.

Similar instrumental analyses by γ-ray spectroscopy to perform semiquantitative analyses of available silica showed degrees of purity represented by the data in Table 4.   These initial surveys of readily available glass-making raw materials showed them to be insufficiently pure for optical waveguide use. In the case of silica, the semiquantitative survey reported in Table 4 indicated that Fe contamination in all of the commercially available powdered silica exceed tolerance limits. Although synthetic fused silica rods (Suprasil) were the purest form of silica available commercially and appeared to meet specifications for most elements, powdered starting materials were required for the production of bulk glass by melting techniques.

TABLE 4.   Detection of trace elements in silica[a]

Supplier	Concentration µg/g		
	Fe	Co	Cr
(1)	1.24	0.030	1.90
(2)	0.82	0.005	2.16
(3)	1.60	0.041	0.17
(4)	1.00	0.008	0.19
(5)	0.68	0.009	0.009
Suprasil	ND	ND	ND
	<0.1	<0.003	<0.005

[a]Semiquantitative γ-ray spectrometric surveys using
 synthetic comparison standards

PURIFICATION METHODS

When readily available commercial raw materials are not sufficiently pure to
meet waveguide tolerance limits for trace impurities, materials of sufficient
purity must be prepared specifically. This project was attacked by a special
task force consisting of purification specialists and analytical chemists
with expertise in quantitative, ultratrace, inorganic analyses. Appropriate
purification schemes had to be devised and evaluated for producing the
desired reagent. Radioisotope techniques and activation analyses were power-
ful tools for establishing optimum conditions for executing the procedure and
for pinpointing specific deficiencies of each step of the purification
process.

Solvent extraction
Solvent extraction is an excellent method for preliminary purification of
reagent grade solutions of sodium or calcium. The efficiency of step A
(Fig. 4) was evaluated by measuring distribution ratios for Cu, Fe, Cr, Mn,
Co, and V using appropriate radioisotopes. The measured distribution ratios
and the corresponding data showing percentage extraction results indicated
excellent removal of trace quantities of Mn, Co, Fe, and Cu from sodium feed
solutions. but the distribution ratios for Cr^{3+} and VO_2^+ were low. Cr^{3+}
could not be 100% extracted with a 0.2% solution of pyrrolidinedithiocarbamic
acid (HPDC) in $CHCl_3$ (6N HCl to pH 3.04), with dithizone, or with
 0.01-0.1 $\underline{M}$ 8-hydroxyquinoline in $CHCl_3$ at any pH.

Other investigations with radiotracers aided in evaluating solvent extraction
methods for preparing ultrapure calcium carbonate. Multiple extraction of
5.0 $\underline{M}$ calcium nitrate solutions with $CHCl_3$ containing 1% dithiocarbamate
showed effective removal of ng/ml amounts of Fe^{3+} and Mn^{2+}. Distribution
ratios at pH 7.4 were ~14 and 900 respectively. This extraction system was
used effectively to decontaminate calcium solution containing Mn impurities.
Samples of an original and extracted calcium solution were irradiated. ^{56}Mn
and ^{64}Cu were separated simultaneously by extraction into $CHCl_3$ solutions of
8% HPDC-0.12% dithizone. Results by activation analysis showed 109 $\pm$ 10 ng
and <0.1 ng of Mn in the original and purified solutions. Copper was below
detection limits in both samples.
Ion exchange
Ion exchange procedures are very effective for removal of ultratrace
impurities. A flow diagram of a procedure for preparing sodium carbonate is
shown in Fig. 4. Procedures of this kind require many handling steps and
chemical manipulations. Therefore, extreme care is necessary to minimize
contamination from containers and to ensure that the most pure chemical
reagents are used. Other major sources of impurities, for example, the
reagent grade $NaNO_3$ feed solution and exchangeable cationic impurities on the
Amberlite IR 120 resin, must be recognized and minimized. Steps A and C were
designed to purify the feed solution and to remove impurities from the loaded
ion exchange resin. Ion exchange resins were also purified by elution with

EDTA prior to loading with feed solutions.

```
                            (1)
                  ┌──────────────────┐
                  │   NaNO₃  SOLN.   │
                  │    300gm/ℓ       │
                  │  REAGENT GRADE   │
                  └──────────────────┘
                          │ FILTER
                          ▼       (2)
                  ┌──────────────────┐
                  │   BOIL  WITH     │
                  │   H₂O₂ HAC       │
                  └──────────────────┘
                          │ EXTRACT
                          │ 5 TIMES
                          │ WITH    (3)
                  ┌──────────────────┐
                  │ CHCℓ₃ SOLN. OF   │
                  │ OXINE (10 gm/ℓ)  │◄──── A
                  │ DITHIZONE (2gm/ℓ)│
                  │ HPDC (10gm/ℓ)    │
                  └──────────────────┘
                          │       (4)
                  ┌──────────────────┐
                  │    EXTRACT       │
                  │    TWICE         │
                  │   WITH CHCℓ₃     │
                  └──────────────────┘
                          │ FILTER
                          ▼      (5)                   (6)                    (7)
   B ──►  ┌──────────────────┐   ┌──────────────┐   ┌──────────────┐
          │ LOAD AMBERLITE IR-│  │  WASH WITH   │   │  WASH WITH   │
          │ 120 CATION EXCHANGE│─►│  6 COLUMN    │──►│  6 COLUMN    │
          │ RESIN, 40-50 MESH │   │  VOLS. EDTA  │   │  VOLS. EDTA  │
          └──────────────────┘   │ (1gm/ℓ) pH 7.0│  │ (1gm/ℓ) pH9.0│
                                 └──────────────┘   └──────────────┘
                (10)                    (9)                    (8)
       ┌──────────────┐       ┌──────────────┐       ┌──────────────┐
       │  CONCENTRATE │◄──────│  STRIP WITH  │◄──────│    WASH      │
       └──────────────┘       │ 2M (NH₄)₂CO₃ │       │    H₂O       │
              │ SATD. CO₂ GAS  └──────────────┘       └──────────────┘
              ▼      (11)               ▲ D
       ┌──────────────┐
       │ PPT. NaHCO₃  │
       └──────────────┘
              │ WASH DRY AT 120°C
              │ IGNITE 300°C
              ▼      (12)
       ┌──────────────┐
       │   Na₂CO₃     │
       └──────────────┘
```
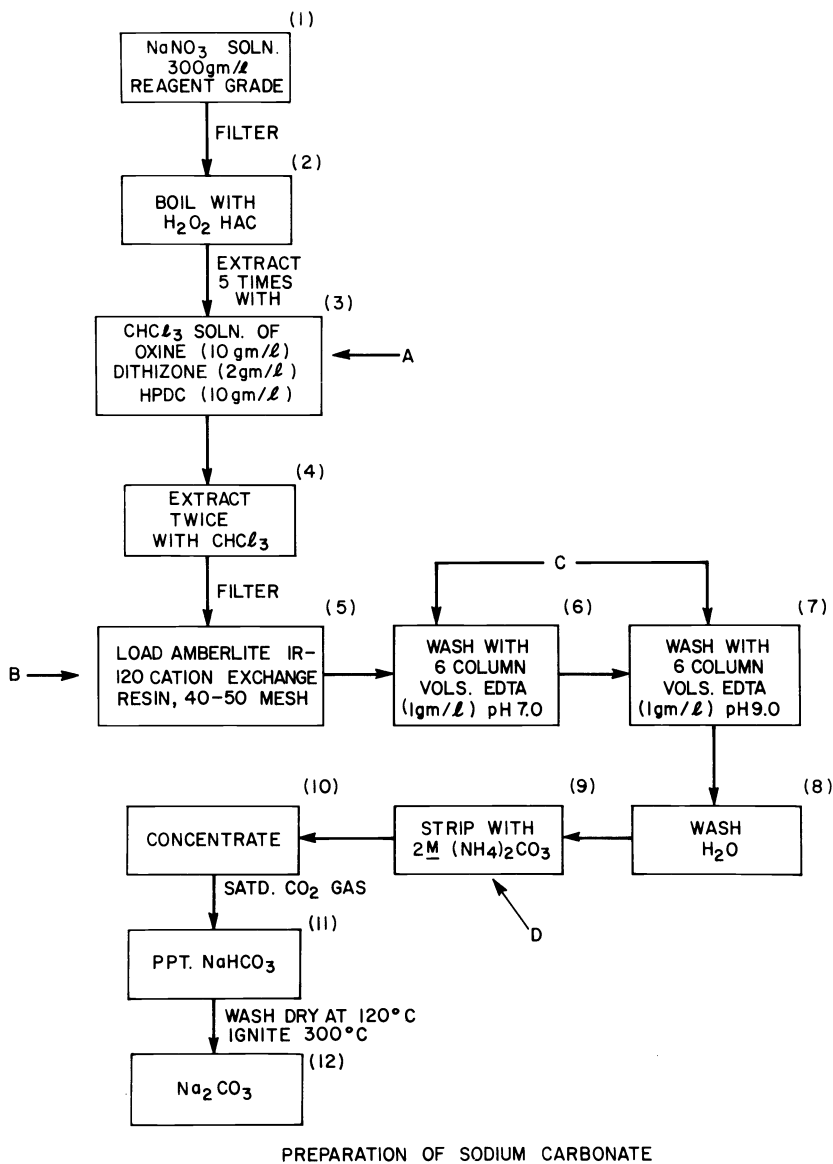
PREPARATION OF SODIUM CARBONATE

Fig. 4.   Solvent extraction and ion exchange scheme for
purifying sodium solutions

The effectiveness of the entire procedure for removing submicrogram/ml
amounts of Fe, Mn, Cu, Cr, Co, and V was determined by radioisotope tech-
niques. One portion of a prepurified sodium nitrate feed solution was doped
with carrier-free or high specific activity ^{59}Fe, ^{54}Mn, ^{51}Cr, and ^{60}Co and
the second aliquot with ^{64}Cu and ^{48}VO$_2^+$. The effectiveness of each step of
the procedure from the purification of the feed solution by solvent
extraction (A) to stripping of the loaded sodium resin with 2M ammonium
carbonate (D) have been examined and detailed experimental procedures and
important results of this investigation are reported elsewhere (Ref. 1).

Mercury cathode electrolysis
Methods based on mercury cathode electrolysis have been perfected as final
processes for decontaminating sodium and calcium solutions (Ref. 2). The
development of the successful procedure for preparing large quantities of the
material depended ultimately on effective analytical support. Small 100g
test samples of CaCO₃ (1 and 2 Table 5) were obtained for evaluation of
purity prior to the beginning of large scale preparations. Neutron activ-
ation results for Mn and Cu showed test samples to pass specifications for

these traces.

TABLE 5.   NAA determination of Mn and Cu in $CaCO_3$

Sample	Conc. found, ng/g	
	Cu	Mn
1[a]	N.D.[b]	43.8 ± 7.8
2	26 ± 6	29.8 ± 1.0
3	N.D.	340 ± 9.0
4	38 ± 5	523 ± 12
5	N.D.	658 ± 13

[a] 4 detn., [b] not detected.

When kilogram quantities of the reagent were supplied (samples 3, 4 and 5)
the level of contamination by manganese made the material unsuitable.
Optimization of the conditions for purification of solutions by mercury
cathode electrolysis has been accomplished by applications of radioisotope
techniques (Ref. 3).   The simultaneous γ-ray spectrometric monitoring of the
removal of impurities from sodium carbonate solutions is shown in Fig. 5.
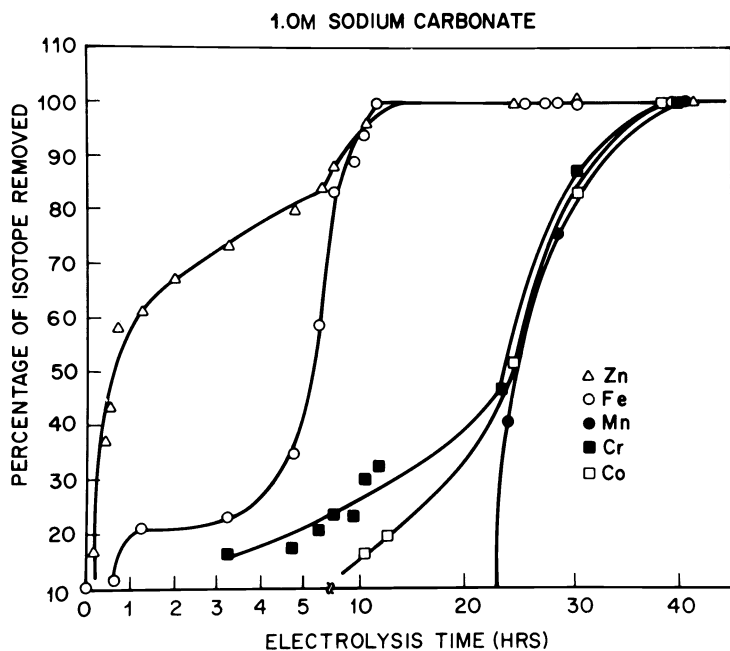
Fig. 5.   Gamma-ray spectrometric monitoring of the mercury
cathode electrolysis purification of sodium carbonate
solutions

Data from these types of studies and that obtained via direct monitoring of
the Mn levels in samples periodically removed during the electrolysis of non-
isotope doped solutions pinpointed the pH and electrolysis time periods

required for efficient removal of ultralow levels of manganese. Accurate con-
trol of the pH and time of electrolysis resulted in large scale preparation
of calcium **carbonate** which passed the specification for manganese. An
additional essential factor in ultrapurification was adequate control of
particulate contamination. XRF and AAS techniques disclosed the significant
contribution of particulate contamination to the total transition element
content of the final product (Ref. 4).

Low temperature sublimation
New technology for optical waveguide production has exploited the vapor phase
oxidation of gaseous molecules, for example $SiCl_4$, $GeCl_4$, $POCl_3$ and BCl_3,
inside fused silica tubes as a process for producing glass (Ref. 5). This
modified chemical vapor deposition (MCVD) process (Ref. 6) thus stimulated
the development of additional methods for the purification and analysis of
CVD reagents. An extremely effective low temperature sublimation technique
was developed for the ultrapurification of a number of important liquids used
as either analytical or MCVD reagents (Table 6).

TABLE 6. Desirable ultrapure reagents

For analytical chemistry

Hydrogen peroxide	H_2O_2
Hydrazine	NH_2NH_2

For chemical vapor deposition

Phosphorus oxychloride	$POCl_3$
Antimony pentachloride	$SbCl_5$
Phosphorus tribromide	PBr_3
Arsenic trichloride	$AsCl_3$
Tungsten hexafluoride	WF_6
Silicon tetrachloride	$SiCl_4$
Germanium tetrachloride	$GeCl_4$
Boron trichloride	BCl_3

Experimental verification of the extremely high efficiency of the method for
the purification of hydrogen peroxide was reported previously (Ref. 7).
Analytical results for the purification of a number of important chemical
reagents is given in Table 7. The low temperature sublimation technique is
now applied for the batch-scale production of kilogram quantities of MCVD
reagents

QUANTITATIVE ANALYSIS OF HIGH PURITY MATERIALS

The production of ultrapure reagents depended critically on high sensitvity
and very reliable quantitative analyses. To obtain the required information
chemical separations and procedures for post irradiation processing of raw
materials were devised. The radionuclidic interference from ^{24}Na during the
determination of Cu and Mn in sodium carbonate was eliminated by passing
carrier-doped solution through hydrated atimony pentoxide (HAP) columns to
remove ^{24}Na. Interferences from other matrix isotopes are eliminated by
simultaneously extracting ^{64}Cu and ^{56}Mn at pH 6 to 8 into $CHCl_3$ containing
1% pyrrolidine dithiocarbamic acid and 0.01% dithizone (Ref. 8). Cu and Mn
in samples of calcium carbonate have been determined in a similar manner. It
was not necessary to remove high levels of ^{24}Na with the HAP column since the
organic extracts of dissolved calcium carbonates contained only low background
activity from this matrix isotope.

The reliability of procedures has been assessed by performing replicate
analyses (6 determinations) of synthetic standard solutions prepared by

dissolving extremely pure sodium carbonate ([Cu] = 18.9 + 7 ng/g, [Mn] = 3.3 + 0.7 ng/g) and doping with with 1.00 μg/ml of Cu and 0.1107 μg/ml of Mn. The results, 0.992 + 0.055, and 0.1050 + 0.035 μg/ml for Cu and Mn respectively indicate errors of 0.8 and 5.3%. Measurable detection limits of 0.3 and 0.03 ng were obtained for Cu and Mn respectively under conditions of 15 min. counting intervals on a 9% efficient sodium iodide well-type detector.

TABLE 7. Results of single sublimations (concn ng/ml)

Impurity	Hydrogen Peroxide[A]		Phosphorus Oxychloride[B]		Hydrazine[B]	
	Before	After	Before	After	Before	After
Co	1000	0.4	< 0.4	N.D.[C]	40	N.D.
Cr	1000	< 2	28	N.D.	127	N.D.
Cu	1000	< 2	N.D.	–	3.0	0.3
Fe	1000	< 2	433 + 6	23 + 8	41	2.0
Mn	1000	0.9	14	N.D.	2.0	N.D.
Ni	1000	–	1245 + 70	N.D.(<1)	13	N.D.

[A]Analyzed by radiosotope method, [B]analyzed by atomic absorption.

[C]N.D. = below detection limits.

For determinations of manganese in calcium carbonates a new substoichiometric method was developed (Ref. 9). With this method highly sensitive, precise analyses with good accuracy were obtained as indicated by the mean of five determinations, 0.151 + 0.009 μg. Comparison of the determined value with that calculated from the recommended SRM value, 0.17 + 0.013 μg, indicated an absolute error of 5.9 to 11.7% for the determination of Mn at the 0.2 μg level.

Additional data on calcium carbonate purity with respect to Cu and Mn are given in Table 5. Other trace elements in sodium carbonate with long lived isotopes, ^{60}Co, ^{51}Cr, and ^{59}Fe, for example, can be measured instrumentally following 100 hr. irradiations at a neutron flux of 2 x 10^{13} n/cm^2 sec and 10 to 20d decay periods. Detection limits of 120, 2, and 0.5 ng were indicated by measuring respective activities from appropriate photopeaks of ^{59}Fe, ^{51}Cr, and ^{60}Co induced in synthetic standard solution.

The determination of these traces in calcium carbonate is complicated by the decay of the matrix isotope ^{47}Ca. Although the matrix isotope could be allowed to decay before measuring low levels of activity from ^{59}Fe, ^{51}Cr, and ^{60}Co, separating matrix isotopes chemically permits analytical results to be obtained more quickly. Sc and Ca have been removed by extraction with TOPO-cyclohexane and HTTA-TOPO-cyclohexane respectively. Carbonates of sodium and calcium analyzed via these methods have usually shown levels of Cr, Co and Fe below detection limits (Ref. 8).

Instrumental gamma-ray spectroscopy has proven extremely useful for screening high-purity silica because of the favorable nuclear decay of the matrix. Characteristic photopeaks can often be assayed immediately after irradiating the samples. The spectra of the sample in Fig. 6 were recorded 24 hrs. after the end of a 100-hr irradiation. In spectrum A ^{82}Br, ^{24}Na, and ^{51}Cr are visible. After decay of the more abundant shorter lived radionuclides, spectrum B was obtained by counting for 23 minutes. Characteristic photopeaks of ^{59}Fe, ^{60}Co, and ^{51}Cr are more distinct than observed in spectrum A.

Cu and Mn in silica can be determined quantitatively after 15 or 30 min. irradiations and volatilization of ^{31}Si by HF. After 100-hr. irradiations and 2-day decay periods, Cr and Co are assayed nondestructively, while up to 60 day irradiations are necessary to increase detection limits for Fe.
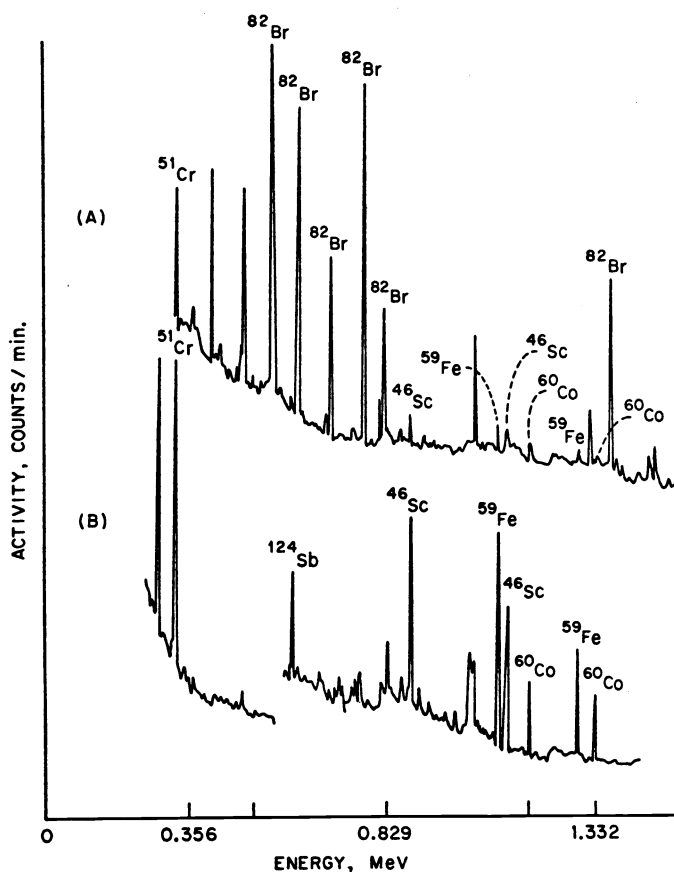
Fig. 6. Gamma-ray spectra of silica

The reliability of instrumental methods should be assessed by analyzing standard reference materials. Results for the analysis of SRM 112 (a silicon carbide) and SRM 85B (an aluminum alloy) are reported in Table 8. Reasonable precision and acceptable accuracy are shown for the determination of relatively large amounts of Fe and Co.

TABLE 8. Fe and Co content of silicon carbide (SMM 112) and aluminum alloy (SRM 85B)[a], μg/g)

	SRM 112		SRM 85B	
Sample	Fe	Co	Fe	Co
Mean of 6 detn.	4570 ± 230	2.50 ± 0.13	2320 ± 50	1.48 ± 0.03

[a]Certified Fe values, SRM 112, 4500 μg/g
SRM 85B, 2400 μg/g

The precision for iron determinations in SRMs 112 and 85B is ±5% and ±2.1% respectively as measured by relative standard deviations. The average absolute error of the value determined for SRM 112 was 2.5% compared to the recommended NBS value. Based on the certified value for SRM 85B an absolute error of 4.6% occurred. Accuracy of the results for cobalt could not be

assessed since no certified data were available. However, the accuracy of
these measurements should be similar to that obtained for iron in view of the
comparable precision for cobalt determinations at much lower levels than iron.

Using the instrumental methods described above, measureable limits for trace
elements in fused silica were 1.0, 0.1, .01, and 30 ng for Cu, Mn, Co, Cr,
and Fe respectively. During most analyses very low levels of Cu and Mn were
found. One example of results obtained by neutron activation for the determ-
ination of various elements in silica prepared by special procedures is
listed subsequently: Cr (0.008 μg/g), Co (ND = <0.001 μg/g), Cu (0.009 ±
.004 μg/g), Fe (<0.100 μg/g), and Mn (0.0089 ± .004 μg/g). Other results
obtained after concentration of trace impurities and measurement by X-ray
fluorescence indicated 0.008, 0.001, 0.03-0.09, and <0.01 μg/g of Cr, Co, Cu,
and Mn respectively. The supplier's emission spectrographic analysis of this
sample after preconcentration of trace elements showed Cr, <0.01; Co, 0.01;
Cu, 0.01; Fe, 0.01; Mn, 0.007; Ni, <0.01; and V, <0.01 μg/g.

Extremely pure raw materials have been prepared successfully and analyzed by
the methods described previously. Additional data for purity characterizati-
ons are reported in Tables 9 and 10.

TABLE 9. Transition metal impurities in silica (ng/g)

Sample[a]	Cu	Mn	Co	Cr	Fe
1A	ND	13	1.0	86	ND
B	18	2.0	1.1	17	ND
C	34	5.8	2.2	37	10^3
2A	50	2.8	1.5	ND	ND
B	41	1.7	1.4	ND	ND
3A	79	2.7	1.0	5.6	ND
B	43	3.4	0.5	ND	ND
C	28	6.3	0.5	ND	ND
C	36	0.5	0.2	2.2	150
4A	35	0.9	ND	1.1	ND
B	12	0.4	ND	1.5	ND
C	15	1.9	ND	1.4	ND
D	45	0.9	ND	ND	ND

[a]A, B, C designates separate analyses of various large batches of
silica obtained from the same supplier.

The results for these materials are reported in chronological order with
respect to the sequence of their preparation in the laboratory. With few
exceptions, the results for silica indicate that specifications were being
met for Cu, Mn, Co, and Cr. Although no clear trend of increasing purity
with time of preparation is seen, silica of extreme purity was obtained
routinely. In contrast to the high-purity of silica, samples of the carbon-
ates (Table 9) have Cu (usually above specifications) and periodic Mn con-
tamination. Sodium carbonates [(1) and (2)] and calcium carbonates
[(1)-(4)] were prepared during the period in which the purification processes
were carefully monitored by analysis at various steps. Preliminary samples
were analyzed also prior to the delivery of the large sample. Very low
levels of impurities were found in these samples, whereas the remaining
samples (Table 10) of sodium carbonate were highly contaminated with Cu.
Most of these samples were delivered without any prior analyses.

For quantitative determinations of trace elements in volatile halides, of Si,
Ge, P, B and As graphite furnace atomic absorption spectroscopy (AAS) was the

preferred technique.

TABLE 10. Transition metal impurities in waveguide raw
materials, (ng/g)

Sample	Cu	Mn	Co	Cr	Fe
Na_2CO_3					
(1)	38 ± 8	46 ± 8	-	-	-
(2)	18.9 ± 7	3.3 ± 1.7	-	-	-
(3)	303	ND	1.0	43.0	ND
(4)	17.7	ND	ND	0.6	ND
(5)	104 ± 4	2.5 ± 0.3	ND	21 ± 2.0	ND
$CaCO_3$					
(1)	-	-	ND	12 ± 4	ND
(2)	-	-	ND	17 ± 3	ND
(3)	ND	35.7 ± 4.2	-	-	-
(4)	26 ± 6	29.7 ± 1.1	-	-	-
(5)	65	ND	<1	ND	ND
(6)	64 ± 3	3.8 ± 0.2	ND	147	ND

[a] Not detected <1.0, <0.1, <0.1, <1.0 and <200 ng for Cu, Mn,
Co, Cr, and Fe respectively.

Reliable procedures were developed for processing samples prior to analysis
with minimum contamination and without loss of trace elements (Ref. 10). In
these reagents iron was the most prevalent impurity and the bulk of all trace
transition element impurities was confined to particulate matter contamination
in the reagent rather than being solubilized in the liquid reagent. Measure-
ment limits for the AAS technique were ~1, 0.3, 0.5, 0.2, 0.5, and 0.5
ng/g for Fe, Cr, Ni, Mn, Cu and Co respectively.

In the sub-ng region quantitative determinations of iron in silicon tetra-
chloride have been based on laser intracavity absorption spectrometry. An
analytically useful laser intracavity spectrometer has been described
(Ref. 11) and its application to quantitative determinations of iron has been
reported (Ref. 12). A key to the successful exploitation of the inherent
sensitivity of the intracavity method for practical analysis was the ultra-
purification of analytical buffer and redox reagents used in the spectro-
photometric procedures (Refs. 12,13).

CONTAMINATION PROBLEMS

During glass melting

In order to perfect techniques for glass-making material scientists performed
exploratory glass-melting experiments using impure reagents. As anticipated,
glasses with absorbance losses in the 200-600 dB/Km range were fabricated.
The gamma-ray spectrum of a sodium-calcium-silicate glass synthesized from
raw materials from a single supplier is given in Fig. 7. The presence of
silver was unexpected and both Cr and Co were well above tolerance limits.
One of the better optical quality samples (still well above the desired
10 dB/Km), prepared from materials from another source, gave the gamma-ray
finger-print shown in Fig. 8. Characteristic photopeaks of ^{51}Cr, ^{192}Ir,
^{124}Sb, ^{46}Sc, ^{65}Zn, and ^{60}Co are present in the glass, but no ^{192}Ir was
detected in any of the spectra of the raw materials used in preparing this
sample. Samples of platinum from crucibles used in the melting operation
were irradiated and substantial activity (> 10^6 counts/min per 100 mg of Pt)
from ^{192}Ir was detected. Gamma-ray spectrometric analysis of glasses melted
in an oxygen atmosphere also contained photopeaks of iridium. However, in

nitrogen atmospheres less irridium was detected in the glass. Thus, prep-
aration of glasses by melting in a nitrogen atmosphere reduced contamination
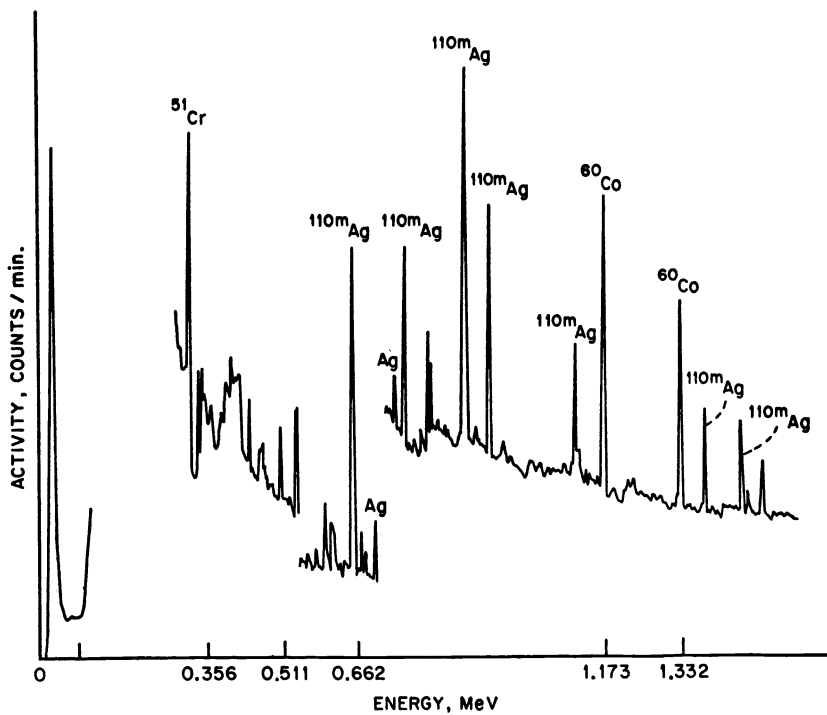from platinum vessels.

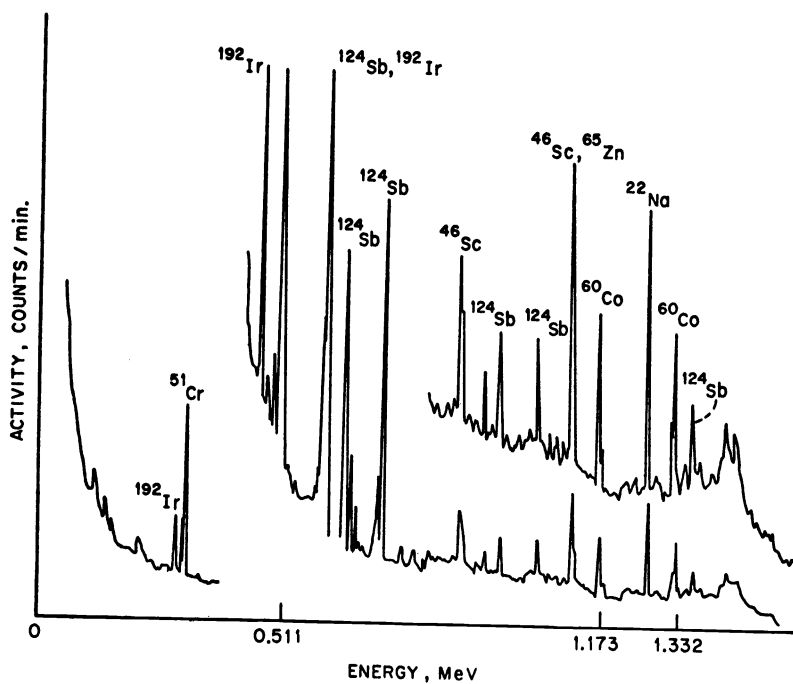Fig. 7. Gamma-ray spectra of Na-Ca glasses.

Fig. 8. Gamma-ray spectrum of glass

During fiber production

Modified chemical vapor deposition (MCVD) methods are now being used
routinely for the production of preforms from which optical waveguide fibers
are drawn (Ref. 5). In this method suitable volatile compounds of silicon
plus phosphorus, germanium, or boron are thermally decomposed to form oxide
composites inside fused silica tubes. Initially during these investigations
some fibers occasionally failed to meet stringent specifications and
causative factors were sought by performing neutron activation analyses. The
most probable suspects were contaminants present initially in the MCVD
starting materials and surface contaminants in the silica tube. The source
of optical loss was investigated as follows. Two tubes of approximately
equal size (0.63 cm x 8.16 cm), one with a thin film of the CVD deposit,
TiO_2-SiO_2, and the other without were prepared and sealed under the
condition existing during the preparation of fiber preforms. These tubes and
an aliquot of a standard solution containing known amounts of Na, Mn, Cl and
Cu were irradiated simultaneously for twenty minutes. After the irradiation,
sample tubes were immersed in 1:1 HNO_3 and rinsed with water to remove any
contaminants from the exterior surface. One end of each sealed tube was then
carefully opened and each capsule was filled with the same volume of 1:1 HF
and HNO_3. The TiO_2-SiO_2 thin film was completely dissolved during a 5 min-
ute equilibration at room temperature. Gamma-ray spectra of these solutions
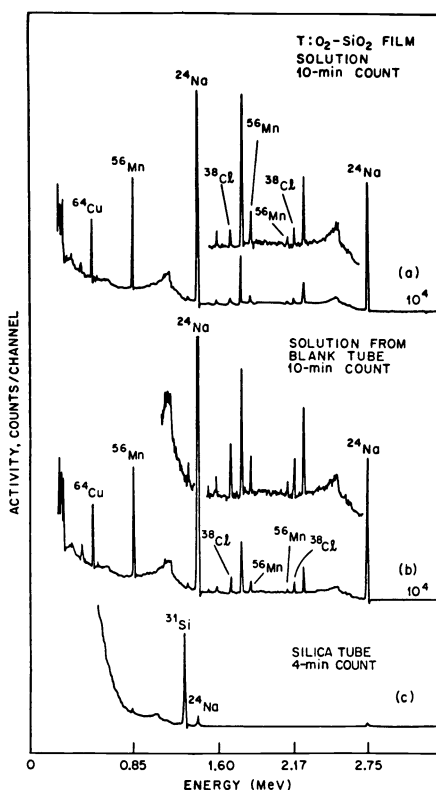are reproduced in Fig. 9(a) and (b).

Fig. 9. Gamma-ray spectra of MCVD film, blank and fused
silica preform tube.

The solution containing the dissolved film was contaminated with 1.3 µg of
Na, 2.5 µg of Mn and 8.6 µg of Cu. Quantities of these impurities in the
solution from the blank tubes were Na = 0.93 µg, Mn = 3.2 µg, and
Cu = 0.15 µg. Thus, excessive amounts of contamination are present already
in the tube prior to deposition of the thin film. A qualitative comparison
of the photopeaks in spectrum (c) shows the concentration of impurities in
the silica tube to be negligible in comparison to the amounts found in the
solutions obtained by rinsing the blank and sample tubes. The results
indicated that more thorough cleaning of tubes prior to MCVD was needed.
Effective procedures for cleaning fused silica tubes serving as containers
for samples during long neutron irradiations have proven to induce negligible
amounts of impurities into contained samples (Ref. 8). Similar procedures
can be adopted for cleaning fused silica tubes used in MCVD production of
waveguides.

In addition to the purity of raw materials and freedom from contamination
during the fabrication of bulk glass, it is also necessary to prevent
contamination when drawing fibers. On one occasion low loss SiO_2 fibers
($\sim$2 dB/Km) were drawn from commercially available pure fused silica and
coated with Teflon (FEP). In a subsequent drawing using identical procedures,
but with a new furnace, a fiber with a loss over 300 dB/Km was produced.
Samples of the acceptable and rejected fiber (15.24 cm lengths x 0.016 cm/dia,
sample wt. $\sim$ 40 mg) were activated to identify the impurities responsible for
high absorbance losses in the bad fiber. Results (ng/g) for good and bad
fibers were respectively Cu, 89 and 311; Mn, 2.2 and 60; and Co <0.1 and 2.2.
The Cr and Fe levels in each fiber were below detection limits of 10 and 200
ng respectively. No W was found in the low loss fiber, but 900 ng/g was
found in the bad fiber. After stripping the FEP coating from a sample of the
high loss fiber and irradiating it, some of the W could be removed by
rinsing the fiber in warm 1:1 HNO_3. This suggested that the impurity was
probably located at the surface of the fiber and was most likely deposited
during drawing. The walls and heating elements of the furnace were con-
taminated with these impurities.

CONCLUSION

Low loss optical waveguides are now being manufactured routinely under fac-
tory conditions in many facilities throughout the world. The rapid progress
in development of these systems has been dependent critically on the devel-
opment of trace analytical techniques for materials characterization and on
new purification methods. Analytical chemistry research in these areas
continues to be vitally important for industrial growth and technological
advancement.

REFERENCES

1. J. W. Mitchell and J. E. Riley, Jr., Practical Application of Neutron
    Activation and Radioisotope Techniques in Optical Waveguide Research
    and Development, Proc. 1976 Int. Conf. Mod. Trends in Act. Anal.,
    Paper B324, September 13-17 (1976).
2. M. Zief and H. Hovath, Lab Practice (1974).
3. J. W. Mitchell and C. McCrory, Reagent Purification by Mercury Cathode
    Electrolysis I: A Practical Guide, in press, Separations and
    Purification Science.
4. J. W. Mitchell, C. L. Luke, and W. R. Northover, Techniques for
    Monitoring the Quality of Ultrapure Reagents – Neutron Activation and
    X-ray Fluorescence, Anal. Chem. 45, 8, 1503 (1973).
5. J. B. MacChesney, P. B. O'Connor, F. V. DiMarcello, J. R. Simpson, and
    P. D. Lazay, Preparation of Low Loss Optical Fibers Using Simultaneous
    Vapor Phase Deposition and Fusion, Tenth Int. Cong. on Glass, Kyoto,
    Japan, pp. 6-40 (July, 1974).
6. J. B. MacChesney and P. B. O'Connor, U. S. Patent 4,217,027, July 31,
    1980.
7. J. W. Mitchell, Purification of Analytical Reagents and Other Liquids by
    Low Temperature Sublimation, Anal. Chem., 50, 194 (1978).
8. J. W. Mitchell, W. R. Northover and J. E. Riley, Jr., Analysis of
    Ultrapure Sodium and Calcium Carbonate by Neutron Activation, J. Radio-
    anal. Chem., 18, 133 (1973).
9. J. W. Mitchell and R. Ganges, Determination of Manganese by Substoich-
    iometric Neutron Activation, Talanta , 21, 835 (1974).
10. T. Y. Kometani, Flameless Atomic Absorption Spectrometric Determination
    of Ultratrace Elements in Silicon Tetrachloride, Anal. Chem., 49,
    2289 (1977).

11. J. S. Shirk, T. D. Harris, J. W. Mitchell, A Laser Intracavity Spectro-
    meter for Analytical Applications, Anal. Chem., 52, 1701 (1980).

12. T. D. Harris and J. W. Mitchell, Sub-part Per Billion Iron Determination
    by Laser Intracavity Absorption, Anal. Chem., 52, 1706 (1980).

13. J. W. Mitchell, T. D. Harris, and L. D. Blitzer, Safe Handling and
    Purification of Aqueous Hydrazine, Anal. Chem., 51, 774 (1980).