ANALYTICAL CHEMISTRY OF FAST REACTOR FUELS — A REVIEW

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Abstract - A mixture of UO_2 and PuO_2 (MOX) has been chosen for use as
fuel in fast reactors. Fabrication technology has been established for the
production of MOX fuel using the method of mechanical blending of UO_2
and PuO_2. Control of trace constituents at different stages of fabrication,
namely blended powder, sintered pellet and the finished pellet is necessary
to obtain the fuel capable of undergoing the designed burn-up without
failure. In this paper analytical methods are described for the trace non-
metallic constituents, trace metallic constituents, stoichiometry and iso-
topic composition. Some of the developments in post-irradiation studies
of fast reactor fuels, particularly fission gas release, migration of non-
gaseous fission products and burn-up are also discussed.

1. INTRODUCTION

Nuclear power is being produced in thermal reactors for more than two decades in many
countries. Most of the thermal reactors in operation at present are of two types - light
water reactors (BWR's & PWR's) using low enriched uranium fuel and heavy water reactors
using natural uranium fuel. It was realised quite early that energy from uranium can be
extracted only to a limited extent with the thermal reactors and the same could be increased
by a factor of 50 by the fast breeder reactor concept since more fissile material can be
produced than what is burnt. With this in view, the development of fast breeder reactors
was initiated in the early 60's.

Now a few countries have experimental and prototype fast reactors either in operation or
under construction. Some experimental fast reactors in operation are KNK-II in FRG,
JOYO in Japan, FFTF in USA and BOR-60 in USSR. In India an experimental fast reactor,
FBTR, is under construction at the Reactor Research Centre, Kalpakkam for the develop-
ment of fast reactor technology. Prototype fast reactors in the world include, Phenix in
France, PFR in UK and BN-350 in USSR. Demonstration fast reactors under construction
are Super Phenix in France, SNR-300 in FRG and BN-600 in USSR.

Work on the fast breeder reactors has been limited to a few countries and has been slowed
down in the last several years due to political and other reasons. Since some countries
consider the plutonium technology as sensitive, information on fast reactor work is not
available freely in open literature. During the International Nuclear Fuel Cycle Evaluation
conducted during 1978 and 1979 various technical aspects of the different nuclear fuel
cycles including plutonium recycle in thermal and fast reactors were analysed. It was
found that fast breeders are necessary and viable taking into account the projected demands
on nuclear power and the availability of uranium. Fast reactors will be of great importance
towards the end of this century particularly for countries with limited resources of both
fossil and nuclear fuels.

Since a wealth of experience has been gained on UO_2 fuel from the operation of thermal
reactors for more than two decades, mixed oxide (MOX) fuel, a mixture of UO_2 and
PuO_2 was chosen for use in the fast reactors and has also been most extensively studied.
Advanced fuels such as mixed carbide, mixed nitride and carbonitride appear to have
some superior qualities, but are still under development.

Analytical chemistry of fast reactor fuels is a wide subject. At the International Sympo-
sium on Analytical Methods in Nuclear Fuel Cycle[1a] held in 1971, a large volume of
information pertaining to plutonium fuels became available. If published literature[1b-1d] is
any indication, it appears that there have been no new concepts or methodology in the past
decade.

As background information, I would refer to the methods for fabrication of fast

reactor fuels. Then I would describe different methods employed for the assay of trace constituents forming part of the chemical quality control. For the sake of completion, I would spend a few minutes on methods for the determination of stoichiometry and isotopic composition.

2.   FUEL FABRICATION

Three different processes have been or are being developed for the production of mixed oxide fuel[1e].

i)   Mechanical blending of UO_2 and PuO_2

This process involves the mechanical blending of ceramic grade UO_2 and PuO_2 powders. Extensive studies[2] have been carried out on this process for fabrication of MOX pellets of required stoichiometry, fissile content, chemical purity, density and dimensions.   Fabrication technology has been improved to meet the stringent specifications. MOX fuel has been fabricated on a ton scale by this process[3,4].

ii)   Coprecipitation

This process involves precipitation of hydrous plutonium oxide-ammonium diuranate mixture from a uranium-plutonium nitrate solution by the addition of ammonia[5,6]. The precipitate is subsequently decomposed thermally and reduced with hydrogen to mixed oxide powder.   Control of precipitation conditions is necessary to obtain homogeneity of U and Pu in the product.   The process has been demonstrated on a multiton production scale .

iii)   Sol-gel processes

In the sol-gel processes, droplets of sol or solution of uranium and plutonium nitrates are converted into gelled microspheres, washed and dried.   The microspheres are then directly sintered and loaded into the clad tubes by vibrocompaction or alternatively pelletised, sintered and the pellets loaded into the clad tubes.

Of the above three routes, the sol-gel route has certain advantages such as 1) minimisation of radiation and contamination problems by elimination of powder handling step, 2) production of microspheres with excellent dissolution properties with even upto a plutonium content of 35%, 3) amenability to remote fabrication and 4) versatility of the process with capability of producing carbide fuel without involving the handling of pyrophoric powders.

Several countries such as FRG, Italy, Netherlands, UK and USA have developed the sol-gel process upto the pilot plant scale, but experience on the performance of this fuel under actual irradiation conditions is somewhat limited.   As the pellets route with its extensive production experience is well established and considerable investments have been already made on the pellet fabrication plants, this fabrication route is not likely to be replaced by the sol-gel route in the near future.   However in countries where new plants are being planned, sol-gel processes may be found more attractive.

3.   QUALITY CONTROL AND QUALITY ASSURANCE

Quality control and quality assurance of fuel are essential before its introduction into a reactor.   Chemical quality control is dependent on the route followed for the fabrication.

3. 1   Chemical Quality Control

Chemical quality control provides a means to ensure that the quality of the fabricated fuel conforms to the chemical specifications for the fuel laid down by the fuel designer The specifications are worked out for the major and minor constituents which affect the fuel properties and hence its performance under conditions prevailing in an operating reactor.   Each fuel batch has to be subjected to comprehensive chemical quality control for trace constituents, stoichiometry and isotopic composition.

Control of trace constituents in the fuel is necessary to obtain the designed burn-up. Fluorine, chlorine and moisture cause corrosion of the clad. Further, moisture can modify the O/M of the fuel and also release hydrogen which can cause pressure build-up. Carbon can react with oxygen forming gaseous carbon monoxide which facilitates transfer of carbon from fuel to the clad causing damage to it. Trace metallic consti-tuents like boron, cadmium and rare earths affect the neutron economy. Control of uranium and plutonium contents and their isotopic compositions is essential in order to ensure the required fissile content. Variations in O/M can affect many properties such as thermal conductivity, melting point, number of phases, chemical reactivity and mechanical strength. O/M has to be maintained in the specified limits of hypo-stoichiometry since the oxygen potential significantly increases with irradiation which may lead to clad corrosion.

Fabrication of fuel pellets starting from sinterable UO_2 and PuO_2 involves steps which are shown in Figure 1[7]. The only specifications of fast reactor fuels available in literature refer to FFTF fuel published in 1971. The specifications for UO_2 and PuO_2 powders and final sintered pellets for the FFTF fuel are shown in Table 1[8]. In this list the lowest tolerance for fuel pellets is for fluorine and lithium namely, 10 ppm, and the highest specification is 500 ppm for Fe, Al, Na, Ni and V. Some impurities may be picked up during grinding, blending, pressing and sintering operations and from the atmosphere with which the powders and the pellets come into contact. Hence, it is necessary to carry out the chemical quality control at different stages of fabrica-tion, namely blended powder, sintered pellet and the finished pellet.

There are some important differences between the chemical quality control of plutonium bearing fuels and that of uranium fuels.

These are:

1. All operations have to be carried out in glove boxes.
2. The quantities of material available are limited and hence sensitive methods have to be developed.
3. Additional analyses have to be carried out in order to ascertain the homogeneity of U and Pu to avoid hot spots, which cause increased local fuel swelling during irradiation.
4. Analytical efforts become more involved since the number of fabrication batches becomes large due to the higher neutron and gamma doses associated with pluto-nium produced in power reactors.
5. Non-availability of adequate standards poses some problems.
6. Plutonium has to be recovered and accounted for after analyses.

3.2 Quality assurance

Quality assurance programme provides the evidence that the quality control function is being performed adequately and the fuel is made to meet the specifications laid down. This is achieved by an independent quality surveillance team. Records maintained on physical and chemical quality control in different stages, samples of actual fuel pellets used, original radiographs of fuel pin welds etc. are scrutinised by the quality surveillance personnel before the fuel is cleared for making final assemblies to be loaded in the reactor.

4. ANALYTICAL METHODS FOR CHEMICAL QUALITY CONTROL

Now I would describe analytical methods in use for chemical quality control in some detail.

Chemical quality control involves sampling, analysis, treatment of data and certifi-cation. After a brief description of sampling I would describe the analytical methods under four subheadings

(i)   trace non-metallic constituents
(ii)   trace metallic constituents
(iii)   stoichiometry
(iv)   isotopic composition

I would then refer briefly to treatment of data.

TABLE 1.   Chemical specifications for FFTF fuel materials[8]

Specifications	Maximum Values (Unless otherwise stated)		
	Ceramic Grade UO_2	Ceramic Grade PuO_2	Mixed Oxide Fuel Pellets
1. Carbon, μg/g	150	200	150
2. Chlorine, μg/g	25	50	20
3. Fluorine, μg/g	25	25	10
4. Nitrogen, μg/g	200	200	200
5. Phosphorus, μg/g	50	200	100
6. Sulphur, μg/g	300	300	300
7. Gas, STP cc/g	None given	None given	0.09
8. Water, μg/g	5000	None given	50 for indiv. pellets; 30 for lot average
9. Metal Impurities μg/g			
Al	500	250	500
B	10	10	20
Be	20	20	20
Ca	100	500	250
Cd	20	20	20
Co	10	20	20
Cr	200	200	250
Fe	400	350	500
K	200	200	200
Li	10	10	10
Mg	25	100	25
Na	500	300	500
Ni	400	300	500
Ta	400	400	400
W	100	100	100
V	400	200	500
$\leq$ Cu, Si, Ti, Zn	800	800	800
$\leq$ Ag, Mn, Mo, Pb, Sn	200	200	200
$\leq$ Dy, Eu, Cd, Sm	100	100	100
10. Pu, wt%	Not applicable	Min. 85.0 at time of packaging. Min. 87.5 after heating to 950°C.	± 3.5 rel% of nominal value for indiv pellets; ± 1.0 rel % nominal value for lot average.
11. U, wt %	Min. 86.6 dry basis	0.2	$\pm$ rel % of actual content
12. O/M Ratio	2.00 to 2.25	1.95 to 2.00	1.94 to 1.97
13. Pu Isotopic, wt %			
239 + 241		88.0 $\pm$ 0.5	88.0 $\pm$ 0.5
241	Not applicable	2.5	2.5
238		0.15	0.15
Sum others except 240		0.35 balance	0.35 balance
14. U Isotopic, wt % ^{235}U	Natural 0.7$\pm$0.05		Natural 0.71 $\pm$ 0.05
15. Americium wt % of Pu	Not applicable	0.25	0.25

TABLE 2. Methods for trace non-metallic constituents

Sr. No.	Element	Method	Principle	Range of trace Constituent, μg	RSD %	Time of Analysis
1.	Carbon	1. Manometry	Combustion to CO_2, condensing in liquid nitrogen, warming to room temp. and measurement of pressure	6-10	5	1 hour
		2. Conductometry	Combustion to CO_2 absorption in $Ba(OH)_2$ solution, measurement of change in conductivity	100-400	10	1 hour
		3. Gas chromatography	Combustion to CO_2, separation by gas chromatography, measurement by thermal conductivity	20-400	2	5 mts
		4. Infra-red	Combustion to CO_2 and measurement by infra-red absorption	-	-	-
2.	Chlorine and fluorine	Pyrohydrolytic liberation and measurement by the following methods:				
		1. Spectrophotometry	Chlorine-formation of red coloured ferric thiocyanate complex and measurement at 460 nm·	10-40	5	1 hour
			Fluorine-Zr-alizarin and measurement at 525 nm.	5-20	15	3 hours
		2. Ion selective electrode	Measurement of potentials of the respective ion selective electrodes	Cl, 10-40	4	1 hour
				F, 4-20	7	1 hour
3.	Nitrogen	1. Kjeldahl	Decomposition of sample with acid, making it strongly alkaline, steam distillation of ammonia into boric acid and spectrophotometric measurement at 410 nm by using Nessler's reagent	40-90	3	5 hours
		2. Inert gas fusion	Fusion of the sample in an inert gas at 3000^oC followed by conductivity measurement	10-80	2	15 mts

Sr. No.	Element	Method	Principle	Range of trace Constituent, μg	RSD %	Time of Analysis
		3. Vacuum fusion	Fusion of the sample under vacuum followed by pressure measurement	100	10	3 hours
4.	Phosphorus	Spectrophotometry	Dissolution, conversion to phosphomolybdate, extraction with n-butanol, reduction and measurement at 725 nm.	5-10	3	3 hours
5.	Sulphur	1. Spectrophotometry	Dissolution, reduction to sulphide and measurement of H_2S as complex of Lauth's violet at 595 nm	600	3	3 hours
		2. Turbidimetry	Conversion to SO_3, and then to $BaSO_4$ and measurement by turbidimetry	40-100	20	3 hours
		3. Infrared	Conversion to SO_2 and measurement by infrared absorption	-	-	5 to 10 mts
6.	Total gas	Manometry	Heating at $1600^{\circ}C$ and measurement of the pressure of gases evolved	0.025 cm^3/g	10	5 hours
7.	Moisture	Manometry	Heating to liberate H_2O, condensing at liquid N_2 temp. and measurement of pressure after warming to room temp.	10-100	10	1 hour
		Coulometry	Heating in flowing inert gas to liberate H_2O; absorption in P_2O_5 cell; electrolysis and integration of current	10	4	1 hour

TABLE 3. Carriers used in Emission Spectroscopy for common elements

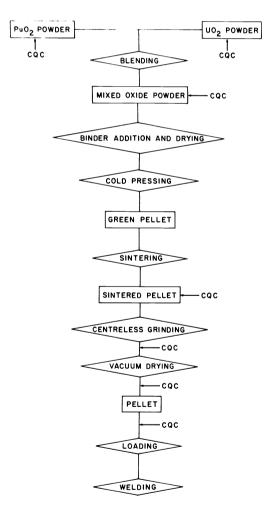| Sr. No.	Matrix	Carrier	Remarks
1.	$(U, Pu)O_2$ and U_3O_8	AgCl	Ag and refractory elements cannot be determined
2.	U_3O_8	$Ga_2O_3 + SrF_2$	Refractory elements cannot be determined
3.	PuO_2	$Ga_2O_3 + NaF$	Refractory and alkali elements cannot be determined
4.	$(U, Pu)O_2$ and U_3O_8	$AgCl + NaF$	Refractory elements are determined. Ag and alkali elements cannot be determined.

FIG.-I. PROCESS FLOW CHART FOR MIXED OXIDE PELLET
Ref. 7   FABRICATION. CQC - CHEMICAL QUALITY CONTROL

4.1 Sampling

The number of samples taken should be statistically significant and it is normally about 10 for a lot of 5,000-10,000 pellets in order to provide reliable estimates of the mean and standard deviation of the specification measured[9]. The samples should retain their integrity during their transport from the sampling point to and storage in the quality control laboratory before actual analysis. Grinding, crushing and pulverising operations, where applicable, must be planned and carried out with great care to ensure that there is no pick-up of impurities.

Specification analysis is carried out at 3 stages of fabrication namely, UO_2-PuO_2 blend, sintered pellets and finished pellets besides UO_2 and PuO_2 feed materials. The pellets are crushed and ground to powder for all the measurements except for moisture and total gas.

4.2 Methods for the Determination of Trace Non-Metallic Constituents

Determination of trace constituents like carbon, halogens, nitrogen, moisture, sulphur, and total gas involves gas-solid reactions and optimum experimental conditions have to be employed to ensure their quantitative recovery. Nitrogen and sulphur are determined by wet methods also. Phosphorus is determined only by a wet method. The methods for trace non-metallic constituents are listed in Table 2.

Carbon

Carbon is converted to CO_2 by combustion of the sample in oxygen atmosphere. In order to effect quantitative and rapid combustion to CO_2, various accelerators such as copper, tin and tungsten have been employed. Manometric[10], conductometric[11], gas chromatographic[10] and infrared absorption[12] methods are employed for the measurement of carbon dioxide.

In the manometric method CO_2 is quantitatively condensed in a capillary tube and its pressure is measured after allowing it to expand at laboratory temperature. The precision of this method is 5% and the time taken is about 1 hour.

In the conductometric method, CO_2 is absorbed in barium hydroxide and the decrease in conductivity gives a measure of carbon content. A precision of 10% is attainable with an analysis time of 1 hour.

In the gas chromatographic method, CO_2 is separated using a silica gel column and its thermal conductivity is measured. A recent improvement in this method is the introduction of rapid heating and measuring devices in commercial instruments which leads to a precision of 2% and an analysis time of 5 minutes.

In the infra-red absorption method, CO_2 is separated and measured. Commercial analysers are available for measuring the infra-red absorption of CO_2 and SO_2 for the simultaneous determination of carbon and sulphur.

Halogens

Chlorine and fluorine in the sample are liberated by pyrohydrolysis as HCl and HF respectively and measured by spectrophotometry[10,13,14,15] or ion selective electrodes[10,13,14,15], or titrimetry[15]. The sample is heated at 900-1000°C in a stream of air or argon saturated with water vapour. The separated fluoride and chloride are collected in an acetate buffer solution. Fluoride is measured using a fluoride ion selective electrode or by spectrophotometry using Zr-alizarin complex. Chloride is measured by spectrophotometry using ferric thiocyanate complex or by titrimetry using constant current coulometry to generate silver ion with amperometric end point detection. Measurement by chloride ion selective electrode is applicable to solutions containing 2 ppm and higher concentrations of chloride. A precision of 5 to 15% is obtained with 5-20 micrograms of chlorine and fluorine. Time taken for analysis is between 1 and 3 hours.

In a recent development the measurement of chlorine and fluorine is proposed to be automated[12]. The halides will be liberated in 30 seconds by pyrohydrolytic fusion.

Gaseous HCl and HF will be separated chromatographically and measured by a gas probe sensitive to halides at ppb levels. The total time required is expected to be 5 minutes or less.

Nitrogen

The most widely employed method for the determination of nitrogen is the classical Kjeldahl's method[10]. It consists of conversion of nitride nitrogen to ammonium salt by refluxing the sample with sulphuric acid and steam distillation of ammonia in alkaline medium into boric acid followed by spectrophotometric measurement[10] using Nessler's reagent. Time taken for analysis is about 5 hours.

In the past two decades inert gas[16] and vacuum fusion[17] techniques have been developed for fast and accurate determination of nitrogen.

The inert gas fusion method consists of fusing the oxide sample rapidly in a graphite crucible using an impulse heating furnace at $2300^{\circ}C$ in a flowing helium atmosphere with a flux of Pt or Ni. The carbon monoxide released is converted to CO_2 by passing through hot CuO and then trapped at liquid nitrogen temperature. Nitrogen and hydrogen are absorbed on a silica gel column at liquid nitrogen temperature. The column is then warmed to $50^{\circ}C$ and the nitrogen liberated is measured by thermal conductivity. A precision of 5% is obtained and the analysis time is about 1 hour.

A temperature of $3000^{\circ}C$ is used in the inert gas fusion method with commercial determinators[12]. In these instruments, removal of CO and H_2 is achieved by converting them to CO_2 and H_2O respectively and absorbing them in ascarite and anhydrone respectively. An improved precision of about 2% is achieved in a short analysis time of 15 minutes.

In the vacuum fusion method, the fusion is carried out in vacuum instead of inert gas atmosphere. The method[17] consists of measurement of total pressure of CO, H_2 and N_2 followed by separation of H_2 by diffusion through a palladium thimble and of CO by conversion to CO_2 and trapping it at liquid nitrogen temperature. The pressure of residual nitrogen is measured. A precision of 10% is reported.

Though commercial instruments employing vacuum fusion technique are available, there is no published data on $(U, Pu)O_2$. Due to the problems associated with the maintenance of high vacuum systems under glove box conditions, inert gas fusion method is preferable.

Phosphorus

Phosphorus is determined by a wet method[10]. The sample is dissolved in HNO_3-HF. After fuming with sulphuric acid the phsophate is converted to ammonium phosphomolybdate which is extracted into n-butanol. After reduction with $SnCl_2$, the optical density of molybdenum blue is measured. A precision of 3% is obtained with 100 micrograms of phosphorus.

Sulphur

Sulphur is measured by both wet and dry methods.

In one of the wet methods[10], the sample is dissolved in HNO_3-HF and converted into chloride. The higher oxidation states of sulphur are reduced to sulphide and the distilled hydrogen sulphide is converted into Lauth's violet, which is measured spectrophotometrically. A precision of 3% is achieved for 600 micrograms of sulphur.

In another wet method, sulphur is converted into SO_3 and oxidation to sulphate is completed by H_2O_2 in alkaline solution. The sulphate is converted into barium sulphate which is measured turbidimetrically. A precision of 20% is obtained with 40 to 100 micrograms of sulphur.

In the dry method, the sulphur is converted to SO_2 by burning the sample in oxygen at $1600^{\circ}C$ with tungsten as flux. A recent improvement[12] over the existing methods is the estimation of SO_2 using an infra-red detector. A precision of 2% is obtained

for sulphur contents of 10 to 400 micrograms with an analysis time of 5 to 10 minutes.

Total Gas

Total gas is determined by heating the sample in vacuum and measuring the pressure of the released gas[10, 15, 18]. It has been reported that no evolution of gases occurs above 1600°C from UO_2-PuO_2 pellets[18]. The recommended procedure consists of heating the sample at 1600°C in a tungsten crucible, removal of water in a cold trap and measurement of the gases evolved at 1600°C using a manometer[10, 15] or electronic pressure gauge[12]. A precision of 10% is obtained at 0.025 cm^3/gram of gas. Rugged commercial instruments employing ultra-high vacuum sample lock are now available. Work is reported to be in progress at Hanford Engineering Development Laboratory for automating the measurement so that the time of analysis can be reduced to 10 minutes[12].

Moisture

Moisture is determined by two methods, namely manometry[19] and coulometry[10, 20].

In the manometric method, moisture is liberated by heating the sample at 400°C in vacuum and then condensed in a liquid nitrogen trap. The trap is isolated, the moisture allowed to expand into a known volume and the pressure measured with an oil manometer, to get a precision of 10% with 10 to 100 micrograms. The analysis time is about one hour.

In the coulometric method the sample is heated at 200°C[15] or 400°C or 1000°C[21], in flowing dry inert gas (argon or nitrogen) and the moisture liberated is absorbed in a P_2O_5 coated cell. Water is then electrolysed and the integrated current gives a measure of the moisture content. A precision of 4% with 10 micrograms of moisture is reported using commercial analysers. The analysis time is about 1 hour.

The temperature to which the sample should be heated needs further investigation since it has been reported that the hypostoichiometric mixed oxide is oxidised by water even at 75°C[21a].

4.3   Methods for the determination of trace metallic constituents

Unlike trace non-metallic constituents which are determined by different chemical methods for each element, trace metallic constituents are determined mainly by emission spectroscopy which is a multi-element method[22]. With the emergence of nuclear technology, emission spectroscopy has undergone phenominal growth in the last three decades with great improvements in the sensitivity as well as its adaptation to complex matrices. The main obstacle encountered in the analysis of U and Pu oxides by direct excitation in a DC arc, is the interference of the spectra of U and Pu with the spectral lines of elements to be determined and the continuous radiation of solid particles of U and Pu oxides which might enter the arc. This obstacle has been largely overcome with the development of carrier distillation method.

This method involves (i) the conversion of sample matrix to a more refractory form : UO_2 to U_3O_8, (U, Pu)O_2 + PuO_2, (ii) addition of a small amount of selected volatile carrier material and (iii) partial distillation of the mixture (sample + carrier) in a D.C. arc using a specially designed electrode assembly. The main function of the carrier is to stabilise the arc at a temperature, where slow release of the trace constituents into the arc is facilitiated, thereby effecting a sharp separation from the refractory matrix. In the choice of carrier materials the volatility and ionization potential are important considerations. In general, the carrier should have an intermediate volatility and an intermediate ionization potential among the group of elements to be determined. Therefore no single carrier is suitable for all elements and suitable mixtures of carriers have been found to optimise the fractional distillation and excitation of a specific group of elements. Gallium oxide, AgCl and their mixtures with alkali and alkaline earth fluorides are among the more commonly used carriers for the determination of trace metallic constitutents other than the lanthanides[23-26]. The details are given in Table 3. Optimum results are obtained by matching the samples and standards as closely as possible in density and chemical form. As lanthanide

oxides are nearly as refractory as U and Pu oxides, carrier distillation method has not been found suitable for their determination at ppm level. They are determined after chemical separation of U and Pu by solvent extraction using TnOA-Xylene/HCl system[27].

The wave lengths, detection limits and estimation ranges for different elements in (U, Pu)O_2 are given in Table 4. The precision of determination with photographic detection is 20-40%. Electrical detection improves the speed and precision of anlayses. The use of direct reading spectrometers with computer based data handling system has been reported[15]. In spite of many advantages they do not have the flexibility on the choice of analytical lines, and commercially available instruments do not have high resolution as they need very high temperature stability. A recent improvement in the spectroscopic techniques is the inductively coupled plasma source which offers a high detectability in the nanogram range, a high precision ($\sim$10%) and rapid analysis. However, U and Pu solutions cannot be directly excited and therefore the trace elements of interest should first be separated from U and Pu.

Atomic Absorption Spectrometry

Another spectroscopic technique offering high precision ($\sim$10%) and sensitivity is Atomic Absorption using flame or electrothermal atomizers. This is a simple and elegant technique needing small sample size (a few mg or ml) and is easily adaptable to glove box operation.

Methods have been developed for the determination of a number of elements such as Cd, Co, Cu, Ni, Mn etc in uranium[28,29] and the technique appears to be promising for plutonium. This will be complementary to the emission spectrographic method. One area where future R & D has to be concentrated is in the development of procedures to effectively atomize B and Gd in AAS which have detection limits of 10-20 ppm under the present conditions.

Spark Source Mass Spectrometry

Spark Source Mass Spectrometry (SSMS) is a powerful technique for the determination of metallic and non-metallic trace constituents present at as low as parts per billion concentrations in various matrices. It has been employed for analysis of U, Pu etc. for the determination of trace impurities.

It requires about 10 milligrams of the sample containing nanogram amounts of the elements of interest. For a survey analysis or measurement of a large number of trace constituents, photographic plate is used as the detection system while for selected elements, electrical detection system is used. The precision is about 25% using photographic plate and about 10% with electrical detection system. A precision of 3-5% has been reported by using isotope dilution SSMS technique for cadmium samples[29a].

SSMS has been used for the determination of trace constituents Ta, W, S, Cl, F, P, Sm, Eu, Gd and Dy in (U, Pu)O_2[15], and for the determination of trace constituents B, Cd, Sm, Gd, Dy in $^{233}UO_2$[30]. A precision of about 25% is reported using photographic plate and this can be improved using isotope dilution technique and electrical detection system.

4.4 Methods for the Determination of Stoichiometry

The concentrations of uranium and plutonium are determined by wet methods after dissolution of the sample and the O/M is determined by dry methods.

Dissolution

Quantitative dissolution of PuO$_2$ and (U, Pu)O_2 samples has received considerable attention[31]. One of the most widely used methods of dissolution is to treat the sample with concentrated HNO_3 and small quantities of HF. The dissolution rate generally decreases with increase in Pu/U ratio. Fusion with ammonium bisulphate and later treatment with H_2SO_4 is another recommended method. Samples which cannot be easily dissolved by these methods have to be subjected to more drastic

TABLE 4.   Wave lengths, detection limits and estimation ranges for trace metallic constituents in $(U, Pu)O_2$

Element	Wavelength A	Det. Limit (ppm)	Estimation Range (ppm)
Ag	3280.7, 3382.9	0.02	0.02-2
Al	2575.1, 3082.2	1	1-100
B	2496.8, 2497.7	0.1	0.1-10
Be	2348.6	0.1	0.1-10
Ca	3158.9	50	50-100
Cd	2288	0.1	0.1-10
Co	2424.9	1	1-100
Cr	2843.3	2	2-200
Cu	2492.1, 2618.4	5	5-250
Dy	3407.8	0.025	0.025-1
Eu	3212.8, 3213.7	0.025	0.025-1
Fe	2617, 2788	5	5-500
Cd	3422.5, 3350.5	0.025	0.025-1
Li	3232.6	2	2-100
Mg	2779	4	4-200
Mn	2576.1, 2949	1	1-100
Mo	3194, 3208	5	5-500
Na	5890, 5896	4	4-400
Ni	3003.6, 3050.8	0.5	0.5-50
Pb	2663	1	1-100
Si	2435	90	90-540
Sm	3321.2	0.1	0.1-5
Ta	2646, 2653	2	2-200
Th	3421, 3292	0.1	0.1-10
Ti	3239	5	5-500
V	3125	1	1-100
W	2551	25	25-1250
Zn	3072	10	10-1000
Te	2383, 2385	5	5-500

TABLE 5.   Methods for uranium and plutonium

Sr. No.	Element	Reaction	Method	Range	RSD	Interference
1.	Uranium	1. $U(VI) \xrightarrow[10M\ H_3PO_4]{Fe(II)} U(IV)$ Destroy excess Fe(II) with HNO_3 in presence of $Mo(VI)$. $U(IV) \xrightarrow{K_2Cr_2O_7} U(VI)$	Potentiometry	2.5 mg	0.2	Br, I, Sn, Ag, V
		2. Same as above	Amperometry	50 10-0.1	0.06 0.1-1	Br, I, Sn Ag, V
		3. Same as above but till the end point the titration followed potentiometrically and the end point detected amperometrically.	Amperometry	1 5	0.09 0.03	
		4. $U(VI), Pu(IV)$ $\downarrow Ti(III)$ $U(IV), Pu(III)$ $K_2Cr_2O_7 \downarrow$ $U(VI) + Pu(IV)$	Amperometry	100	0.2	Cu and Mo in uranium estimation. Te and V in plutonium estimation.
		5. Reduce impurities at +0.085 V $U(VI) \xrightarrow[Hg\ electrode]{-0.325V} U(IV)$ $HClO_4$	Controlled potential coulometry	1-5 mg	0.1-0.2	Mo, Cr

Sr. No.	Element	Reaction	Method	Range	RSD	Inter-ference
2.	Plutonium	1. $Pu \xrightarrow[NaBiO_3]{AgO} Pu(VI)$	Potentio-metry	4 200-400	0.2 0.3-0.07	Cr, Mn, V Ce, Ru, Rh Pt.
		Add excess Fe(II). $Fe(II) \xrightarrow{K_2Cr_2O_7} Fe(III)$				
		2. Same as (1), with AgO as oxidant	Ampero-metry	40	0.05	Ce, Cr, Mn V, Np
		3. $Pu \xrightarrow{AgO} Pu(VI)$ $\xrightarrow{Fe(II)} Pu(IV)$	Ampero-metry	10-20	0.06	Ce, Cr, Mn V.
		4. Same as (3), with modi-fication by selective reduction of the impurities by As(III) in presence of Os(VIII) catalyst.	Ampero-metry	150-200	0.05	
		5. $Pu \xrightarrow{AgO} Pu(VI)$ $\xrightarrow{Fe(II) \text{ (current)}} Pu(IV)$ $\xrightarrow[Ce(IV) \text{ (current)}]{Excess Fe(II) \text{ (current)}}$	Constant current Coulometry	1-5	0.5-01	
		6. $Pu \xrightarrow{0.5V} Pu(III) \xrightarrow{0.8V} Pu(IV)$	Controlled potential Coulometry	1	0.1	
		7. $Pu \xrightarrow[Fe(III)]{Ce(IV)} Pu(VI)$ Destroy excess Ce(IV) at 1.17 V. $Pu(VI) \xrightarrow{0.25V} Pu(III)$ $Pu(III) + Fe(II)$ $Pu(III) \xrightarrow{0.72V} Pu(V)$	Controlled potential Coulometry	6	0.2	
		8. $Pu \xrightarrow[Fe(III)]{HClO_4} Pu(VI)$ $Pu(VI) \xrightarrow[e^-]{0.25} Pu(III)$ $Pu(III) \xrightarrow[-e^-]{0.72} Pu(IV)$	-do-	0.2		
		9. $Pu \xrightarrow{Ce(IV)} Pu(VI)$ Destroy excess Ce(IV) with arsenite in presence of Os(VIII). Excess Fe(II) $Fe(II) \xrightarrow{K_2Cr_2O_7} Fe(III)$	Ampero-metry	50-60	0.2	

treatment and one such method is the sealed tube method[32, 33] in which a mixture of sample and concentrated acids is subjected to high pressure (4000 psi) at a temperature of 350°C. Under such conditions safety precautions are essential with plutonium samples.

Dependence of the rate of nitric acid dissolution of mixed oxide has been studied[34] using material obtained from the three different fabrication processes : mechanical blending, co-precipitation and sol-gel. In the case of mechanically blended mixed oxide the higher sintering temperature and lower the PuO_2 content the more complete is the dissolution. The extent of dissolution also depends on the route followed for the preparation of PuO_2 used in the blended mixed oxide. The mixed oxide pellets made by co-precipitation process dissolve completely and rapidly in nitric acid at different Pu/U ratios and sintering temperatures. Dissolution of pellets made by sol-gel process have been found to be rapid and complete for different Pu/U ratios and sintering temperatures.

Uranium and Plutonium

A number of methods based on redox reactions are available for the precise and accurate determination of uranium and plutonium in solutions[35].

Uranium is assayed by its reduction to U(IV) in concentrated phosphoric acid with ferrous iron. The excess ferrous iron is oxidised and U(IV) is titrated with standard dichromate using potentiometric or amperometric method. Another common method is the controlled potential coulometry involving the reduction of U(VI) at   -0.325V at a mercury cathode.

The existence of plutonium in several oxidation states in solution offers many possibilities for its determination. Methods are available based on Pu(III)-Pu(IV) or Pu(IV)-Pu(VI) couple. Some of the more recent work includes : (i) oxidation of Pu to Pu(VI) with perchloric acid in presence of ferric ions and determination of Pu(VI) by controlled potential or constant current coulometry[36, 36a], (ii) oxidation of Pu to Pu(VI) with Ce(IV), selective destruction of excess cerium(IV) followed by reduction of Pu(VI) to Pu(III) and then oxidation to Pu(IV) by secondary controlled potential coulometry[37], (iii) oxidation of Pu to Pu(VI) with Ce(IV), destruction of excess Ce(IV) chemically in presence of Os(VIII) catalyst followed by addition of a known excess of ferrous and its amperometric estimation[38], (iv) reduction of Pu(III) with cuprous chloride followed by potentiometric titration of excess Cu(I) to Cu(II) and Pu(III) to Pu(IV) to two separate end points with standard dichromate[39] and (v) reduction of Pu and U to Pu(III) and U(IV) respectively by electrolytically generated H_2 and measurement of total of U and Pu and Pu separately by controlled potential coulometry[40].

Some of the methods for the determination of uranium and plutonium are given in Table 5.

Recently x-ray fluorescence method is under investigation for the non-destructive assay of U and Pu in pellets. Though the precision is not comparable to that of the chemical methods, it is capable of automation and can reduce the time of analysis from 2 days to 4 minutes.

Oxygen-to-metal ratio

Thermogravimetric, gas equilibration and EMF methods are used for the determination of O/M ratio.

Of the three, the thermogravimetric method[10] is the most widely employed. It involves measurement of weight change that occurs when an oxide sample is converted to a stoichiometric reference state of O/M of 2.000 by heating it at 800°C for 6 hours in an atmosphere in which the oxygen potential is maintained at approximately -100 Kcal/mole. The precision is 0.001 unit of O/M. One of the recent attempts to automate this method to reduce the analysis time, is the development of a predictive thermogravimetric technique in which initial weight change data are used to predict overall weight change. It is expected that the analysis can be completed in about 6 minutes.

The CO/CO_2 equilibration method is followed mainly at Harwell[41]. In this method the sample is converted to hyper stoichiometric state by adding a known amount of oxygen and then reduced to the reference state of O/M of 2.000 by equilibrating the sample with a mixture of CO and CO_2 in the ratio 10:1 at 850°C. The amount of CO_2 produced is measured. From the amounts of oxygen added and the CO_2 produced, the O/M is calculated. The precision is 0.0005 unit of O/M.

The EMF method has been recently applied to mixed oxide fuels[42]. The difference of the electrochemical potential between the fuel pellet and one of the two standard electrodes (Ni/NiO, Fe/FeO) is measured. A precision of 0.0005 unit of O/M is reported.

The stability of O/M ratio in mixed oxide fuel pins is of interest since loaded fuel pins may be stored for long periods prior to use in reactors. No non-destructive technique with sufficient accuracy is currently available for the determination of O/M in sealed fuel pins. Experiments carried out on storing the loaded pins for over 2.5 years show no significant change in the O/M during storage[43].

4.5   Methods for the determination of isotopic composition

Mass Spectrometry

Isotopic composition of uranium and plutonium in $(U, Pu)O_2$ is carried out by thermal ionisation mass spectrometry following sequential ion exchange separation[10]. The method is highly reliable over the abundance range of 0.01 to 100% extendable to still lower levels, provided mass interference is absent and chemical separations are carefully carried out without cross-contamination.

Present generation mass spectrometers are capable of analysing nanogram amounts of these materials with a precision and accuracy which is ten times superior to that of earlier instruments. This is achieved by close control of the ionisation conditions and sequental peak jumping with complete automation.

Gamma spectrometry

Gamma spectrometric method is being attempted for the determination of isotopic composition of uranium and plutonium. Though it cannot compete with the mass spectrometric method for precision and accuracy, it is useful as a non-destructive method. Measurements have been made on MOX. For $UO_2-12\%PuO_2$, a precision of 0.5% has been reported with a measurement time of 2 hours[44].

Alpha spectrometry

Alpha spectrometry is an alternative to the mass spectrometric determination of isotopic ratios of plutonium and is especially useful for determination of Pu in samples in which the uranium contamination interferes with the mass spectrometric determination. The alpha activity of ^{238}Pu is measured with silicon surface barrier detector and multichannel analyser. The ^{238}Pu abundance is calculated from the alpha spectrum and from mass spectrometric measurements for major plutonium isotopes on a separate portion of the sample. The relative standard deviation is 1% at a ^{238}Pu abundance of 0.01 wt %.

4.6   Method for ^{241}Am

The ^{241}Am content in $(U, Pu)O_2$ is best determined by alpha spectrometry. The determination of ^{241}Am in different plutonium samples with varying isotopic composition of plutonium and having ^{241}Am content ranging from 0.001 to 2.5% by weight of plutonium gives a precision and accuracy of 1%[45].

4.7   Standards

Standard reference materials are required to (1) calibrate analytical methods (2) evaluate the capabilities of analysts and (3) assure the reliability of routine measurements. They are commercially available only for uranium and plutonium contents (chemical) and their isotopic composition (isotopic). Even these are subject to special

export regulations of the concerned countries for plutonium-bearing materials. There are also problems for transporting plutonium containing materials. The non-availability of standards for O/M, moisture and total gas was mentioned in the 1971 symposium and the situation has not changed. The preparation of working standards for a number of trace metallic and non-metallic constituents for use as test samples for laboratory qualification and quality control purposes has been reported in the 1971 symposium[8]. It consisted of the preparation of blends by physical mixing of impurity compounds powders with powder matrices of uranium-plutonium oxide, uranium oxide and plutonium oxide that closely match the composition of the fuel pellets and source materials. The final blends were made from a master blend through an intermediate blend and quartered and sampled for subsequent analysis to verify blend homogeneity. Such blends are not commercially available and it is the responsibility of the quality control laboratory to prepare them.

4.8 Treatment of data

The chemical quality control laboratory generates a vast amount of data, which need to be collected, stored, processed and retrieved by the laboratory as part of its own internal quality assurance programme designed to demonstrate that methods are under control at all times. This internal program must include a documentation system that provides for traceability of each reported result back to primary data. The system must provide for identification and control of each sample from the time it is received by the laboratory until all required analyses are completed. All data obtained from calibration and control standards must be recorded and be easily re-trievable from the system. The internal programme must include provisions for qualifying analysts and for calibrating and controlling all equipment that affects the quality of measurements. Such a programme has been described for surveillance of fast reactor mixed oxide fuel analytical chemistry[46].

A computer system has been described[46a], wherein a control system for fuel manu-facturing stores and processes all laboratory data. The system verifies that the fuel material has been successfully processed through the required operations, chemical sampling frequencies have been met and that all laboratory results are within specifi-cation prior to issuance of a pellet release report. An important feature of this system is the fast analysis and correlation of the results of laboratory analyses including subsequent prompt investigation and corrective actions for anomalies which may occur.

5. POST-IRRADIATION EXAMINATION

One major advantage of fast reactors is the high burn-up (about 100,000 MW D/Te) which is 5-10 times higher than in thermal reactors. Only limited information is available on post-irradiation studies of fast reactor fuels. The fuel elements operate in an environment of high temperature gradients (about $1000°C/mm$)[47]. The life of fuel is limited due to build-up of gas pressure, fuel swelling and corrosion of the clad[48, 49]. Post-irradiation examination is carried out for understanding these aspects through measurements on fission gas (Kr and Xe) release, migration of non-gaseous fission products and burn-up.

5.1 Fission Gas Release

Xenon is formed in appreciable amounts during irradiation of the fuel and the pressure may be as high as 50 atmospheres in a fuel element at 10 atom% burn-up[50]. Such high pressures may lead to creep causing rupture of the fuel clad. Many theoretical models have been postulated to correlate fission gas release with burn-up[51, 52] and post-irradiation examination has yielded experimental data to develop these models.

The fission gases are extracted through a hole drilled at or near the top of the plenum into a system of known volume. Measurement of pressure along with the mass spectrometric data on the isotopic composition and concentration of fission gases gives the quantities of individual fission gases[46, 53]. Alternatively, the pin is equipped with pressure transducers[51] to measure the internal pressure which gives an estimate of the total volume of fission gases released.

5.2   Migration of Non-gaseous fission products

Any attempt to predict distributions of fission products must start with an assessment
of their chemical states. In practice, the most important factor is the fate of the
two oxygen atoms liberated by each fission event. Another factor which must be
considered is the fact that the fission product formation increases the oxygen poten-
tial of the matrix due to higher yields of caesium in the fission of ^{239}Pu compared
to fission of ^{235}U. At higher burn-ups the final oxygen potential is believed to be
buffered by a complex mixture of Cs, Rb and Mo, all of which can form volatile
species and migrate to the fuel/clad interface together with halides and tellurium.
The migrated fission products, particularly caesium, iodine and tellurium in the clad
and the concentration of these elements at the fuel periphery may have deleterious
effects on the fuel element endurance.

Non-destructive gamma scanning[46,53], x-ray radiography[46,54] and electron micro-
probe[46,54] are used to deduce the axial as well as radial migration of fission pro-
ducts. Radiochemical and mass spectrometric analysis[46,53] of the samples obtained
by microdrilling technique offer means to calibrate and confirm the data obtained by
non-destructive methods. Gamma scanning is used to identify the areas where fission
products are concentrated.

It was observed that strontium, zirconium, barium and rare earths do not migrate as
these form refractory non-volatile oxides. Barium and strontium oxides are not
soluble in $(U,Pu)O_2$ and therefore exist as a separate phase in the form of zirconates.
The remainder of zirconium and the rare earths are present as solid solution in
$(U,Pu)O_2$ matrix. Alkali metals, especially caesium which is regarded as the most
aggressive fission product[46,55,56] in clad interaction, form compounds with halogens.
It also forms oxides in the case of hyper stoichiometric fuels and migrates both
axially and radially. Noble metals ruthenium, rhodium and palladium also migrate and
are present as elements. It is difficult to study the halogen distribution in the fuel
pins since there are no   long-lived radioactive isotopes of iodine or bromine and the
stable isotopes are produced in rather low yields.

5.3   Burn-up

Burn-up data can be experimentally obtained by non-destructive gamma scanning as
well as radiochemical and mass spectrometric methods. Of these, gamma scanning is
most useful in obtaining axial and radial burn-up profiles. Radiochemical and mass
spectrometric methods involve quantitative dissolution of the sample[46,57,58]. Radio-
chemical method involves the determination of fission products such as ^{95}Zr, ^{144}Ce,
^{137}Cs, ^{106}Ru, ^{89}Sr and ^{90}Sr and concentrations of uranium and plutonium determined
by mass spectrometry. Triple spike isotope dilution mass spectrometry[59] for
uranium, plutonium and stable fission product burn-up monitor gives the most precise
burn-up of irradiated fuel. ^{148}Nd has proved to be the best burn-up monitor in the
case of the thermal reactor fuels and this has also been proposed for fast reactor
fuels[60]. In addition ^{143}Nd, total neodymium, total rare earths and zirconium have
also been proposed[59] as burn-up monitors. The possibility of using changes in the
isotopic composition of uranium and plutonium for burn-up determination has to be
looked into in the case of fast reactor fuels.

Various studies reported so far on the post-irradiation examination of fast reactor fuels
have been carried out on test fuel pins which have been irradiated either in experi-
mental fast reactors or in thermal reactors under simulated conditions. Many of
these studies have to be corroborated with the real time performance in a fast reactor.

CONCLUSION

I have made an attempt to give a brief account of the status of the methods for the
determination of trace constituents in fast reactor fuels taking MOX as the present
fuel. From the limited information available in literature it appears that there are
no new developments in the basic methodology or concepts during the last 10 years.
Some improvements have been made for the instrumental techniques leading to auto-
mation, reduction in the time of analysis or higher precision. It appears that, in
general, the present capability is satisfactory. Lack of adequate standards seems to
be the only problem. Analytical chemistry played an important role in the develop-

ment and fabrication of uranium fuels for the operation of thermal reactors which are providing nuclear power in a number of countries. The analytical chemists can have a sense of satisfaction for their contributions. With increasing demands on nuclear power, fast breeders are bound to become more and more important towards the end of the present century. Chemical quality control has become an integral part of the development and fabrication of plutonium fuels. Chemical principles used for specification analysis are the classical ones adapted to meet the demands of plutonium fuels for high sensitivity and glove box adaptation etc. As mentioned by several speakers in this symposium already, analytical chemistry has evolved into analytical science by adopting and adapting new concepts and techniques from all other branches of science. Nuclear science and technology made a major contribution towards this evolution. Analytical chemists can look forward to an increasingly important role they have to play in the field of fast reactor technology essential to meet the increasing energy needs of mankind.

Many new and powerful techniques, particularly activation analysis and laser spectroscopy have been referred to in this symposium and some of them, apparently, are capable of detecting individual atoms. I am not sure when they would become applicable to nuclear fuels containing uranium and plutonium. Activation analysis is not applicable to these because of the fission and other radioactive products that are formed in uranium and plutonium. Apparently the existing methods will continue till the other powerful techniques are developed to a stage that they can be used for plutonium bearing materials.

ACKNOWLEDGEMENT

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