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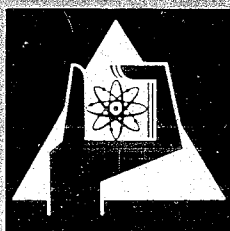
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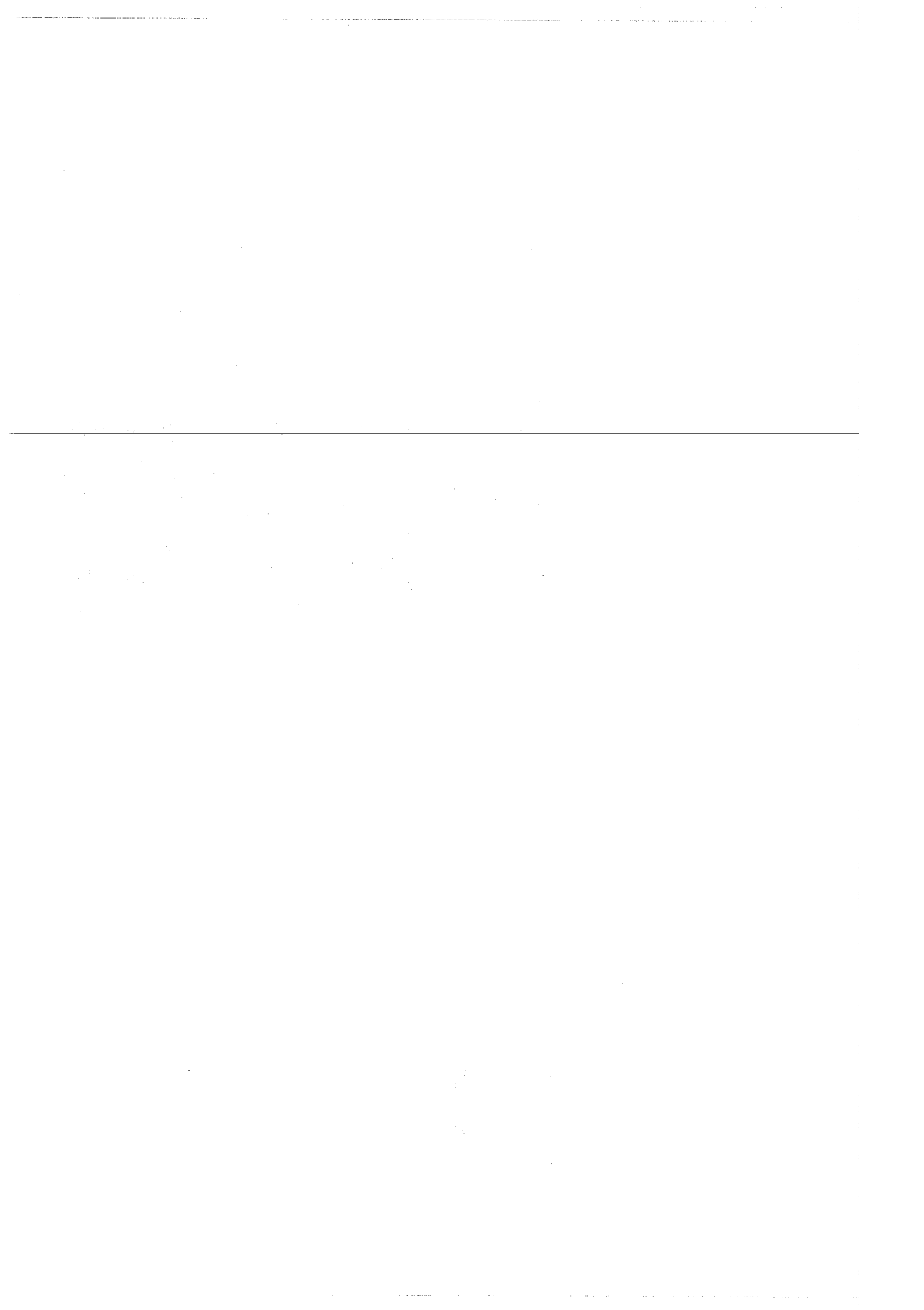
Verification of Input Analysis of a Reprocessing Plant by Means of
Composite Sample Technique

R. Avenhaus, W. Beyrich, L. Koch,
R. Kraemer, D. Thiele, H. Wertenbach



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PLANT BY MEANS OF COMPOSITE SAMPLE TECHNIQUE

by

R. Avenhaus, W. Beyrich, L. Koch,
R. Kraemer, D. Thiele, H. Wertenbach

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2. It is essential to ensure that all financial statements are prepared on a regular basis and are consistent with the underlying data.

3. The second part of the document focuses on the role of the auditor in providing an independent opinion on the financial statements.

4. Auditors are required to follow strict standards and procedures to ensure the reliability and integrity of their work.

5. The final part of the document discusses the importance of transparency and communication in the financial reporting process.

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ABSTRACT +)

The need of batchwise dissolution of reactor fuel elements has the consequence that in principal for establishing the material balance all input batches have to be sampled and analyzed separately. This results in high analytical costs. As only the sum of these data is finally interesting, for reasons of verification the composite sample technique analyzing only one representative mixed 'composite' sample from the input batches may be applied. Let the volume of a single input batch be V_i and that of the corresponding sample taken v_i and γ a constant but arbitrary aliquotation factor such that $v_i = \gamma V_i$. Then the sum $\sum_i v_i = \gamma \sum_i V_i$ is a representative sample of the total input solution and the whole input accountability can be established only by one analysis.

In the experimental realization a remote, motor driven 2 ml burette was taken for pipetting the variable volumes v_i of aliquotes. To avoid cross contamination, the burette was operated according to the Oak Ridge remote pipetter 'Red Oil Method'. In that method the piston of the burette is separated from the radioactive solution by an inert intermediate liquid. The only contaminated part is a siliconized one way tip.

Input accountability during a safeguards experiment in a commercial reprocessing plant by means of composite sample technique showed a difference of 2.5 % both for uranium and plutonium compared with the accountability based on single batch analyses. The inclusion of X-ray fluorescence spectrometry decreased the difference to 2 % for uranium and increased the difference to 3 % for plutonium. As all the values of the uranium and plutonium-concentrations determined by the composite sample technique are higher than those calculated from single batch analyses, it is indicated, that these differences cannot be explained by random errors only. These higher concentrations may be caused for instance by autoradiolysis.

A detailed error analysis for the single batch analyses method as well as the composite sample technique is given.

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Zusammenfassung

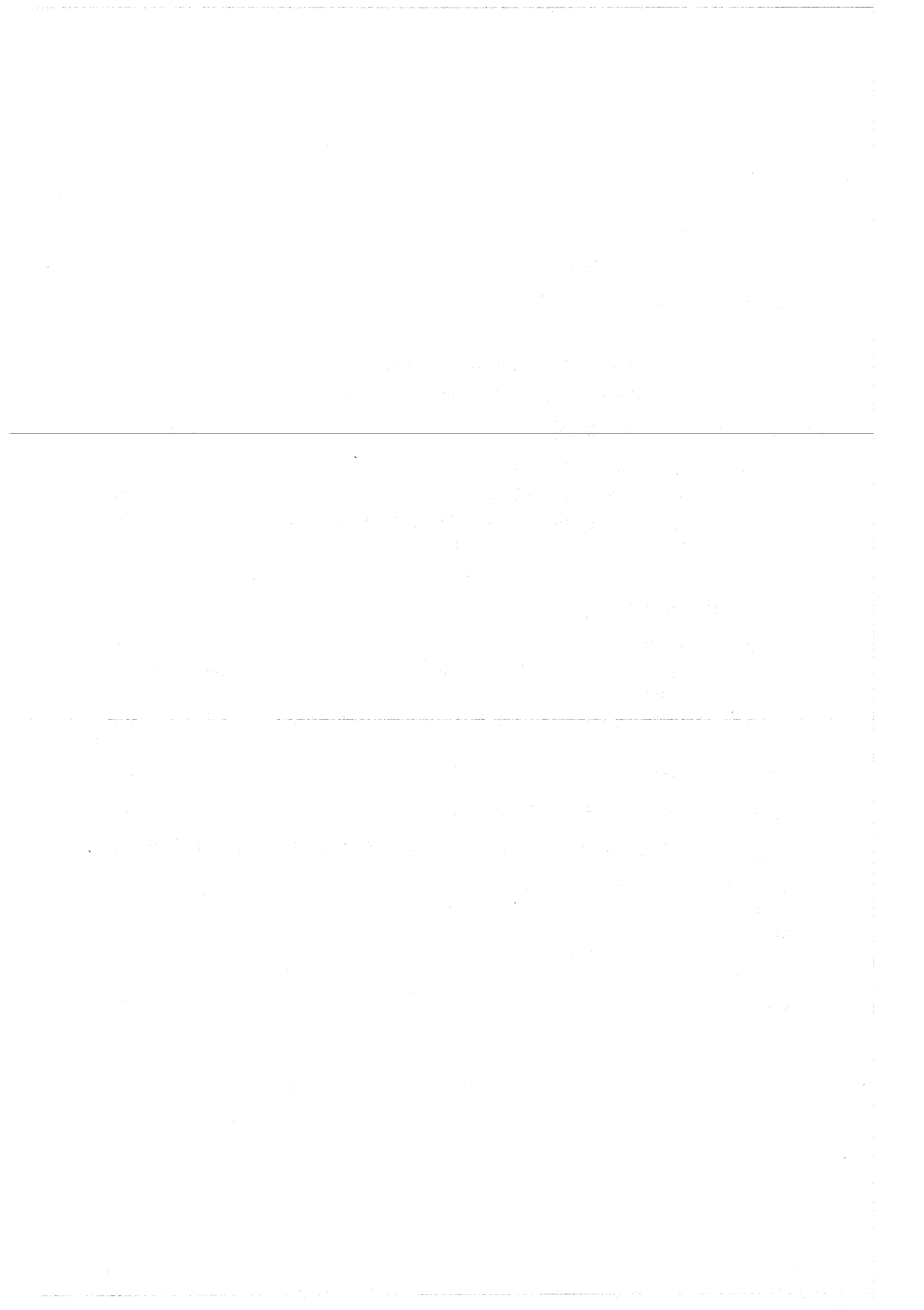
Die Notwendigkeit der diskontinuierlichen Auflösung von Reaktor-Brennelementen hat zur Folge, daß zur Erstellung einer Materialbilanz prinzipiell von allen Eingangsbatches einer Aufarbeitungsanlage Proben gezogen und analysiert werden müssen. Das bedeutet jedoch hohe Kosten. Da nur die Summe aller Meßergebnisse interessiert, kann die 'Composite-Sample-Technik' angewendet werden, bei der nur eine repräsentative zusammengemischte ('composite') Probe analysiert wird. Wenn V_i das Volumen eines einzelnen Eingangsbatches, v_i das der zugehörigen Probe, und γ ein willkürlicher aber fester Aliquotierungsfaktor mit $v_i = \gamma V_i$ ist, bildet die Summe $\sum v_i = \gamma \sum V_i$ eine für die gesamte Eingangslösung repräsentative Probe, d.h. die Bestimmung der gesamten Eingangsmenge kann mit einer einzigen Analyse durchgeführt werden.

Bei der experimentellen Durchführung wurde eine fernbediente, elektrisch betriebene 2 ml Bürette zum Pipettieren der variablen Volumina v_i verwendet. Zur Vermeidung von Kreuzkontamination wurde die Bürette wie der fernbediente Oak Ridge Pipetter nach der 'Red Oil'-Methode betrieben. Bei dieser Methode ist der Kolben der Bürette von der radioaktiven Lösung durch eine zwischengeschaltete inerte Flüssigkeit getrennt. Der einzige kontaminierte Teil ist eine hydrophobisierte Einwegpipette.

Die Eingangsmessung, die während eines Kontrollexperimentes in einer kommerziellen Aufarbeitungsanlage mittels der Composite-Sample-Technik durchgeführt wurde, zeigte einen Unterschied von 2,5 % für Uran und Plutonium gegenüber der Eingangsmessung mittels des üblichen Verfahrens der Einzelanalyse. Die Berücksichtigung der durch Röntgenfluoreszenz-Spektrometrie gefundenen Werte verminderte den Unterschied auf 2 % für Uran und erhöhte den Unterschied auf 3 % für Plutonium. Die Tatsache, daß alle Werte der Uran- und Plutonium-Konzentrationen, die mit der Composite-Sample-Technik gewonnen wurden, höher als die der Einzelanalysen-Technik liegen, weist darauf hin, daß diese Unterschiede nicht nur zufällige Fehler enthalten. Z.B. können diese höheren Konzentrationen durch Autoradiolyse erklärt werden.

Es wird eine detaillierte Fehleruntersuchung sowohl für die Einzelanalysen als auch für die Composite-Sample-Technik durchgeführt.

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1. Introduction

In modern safeguard techniques the establishment of a material balance as accurate as possible gained special importance for the control of fissile material in reprocessing plants [1,2].

The need of batchwise dissolution of the reactor fuel elements has the consequence that in principal all input batches have to be sampled and analysed separately for this purpose. This results in considerable analytical costs especially as because of its high precision until now the rather expensive mass spectrometric isotopic dilution method is the most suitable and therefore most often used analytical technique.

Although batchwise analysis has to be performed by the plant operator for process control anyway and efforts are made to reduce the costs by the complete automation of the analytical procedure [3], there remains the interest in a fast and less expensive method for an independent verification of the operators data.

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3) European Institute for Transuranium Elements (EURATOM), Karlsruhe, Germany
4) now Bundesanstalt für Materialprüfung, Berlin-Dahlem, Germany
5) Institut für Radiochemie, Kernforschungszentrum Karlsruhe, Germany

For this purpose, the "Composite Sample Technique" has been proposed and already used [4,5]: from the sample material of each input batch an aliquote is taken and these aliquots are mixed together. If the aliquotation factor (defined as the ratio of the aliquote volume to the volume of the fuel solution in the tank) is kept constant the concentration of this composite sample is equal to the concentration one would obtain by mixing the fuel solution of all batches together. Therefore, if the input volumina are known, analysis of the composite sample only is sufficient to determine the total amount of uranium and plutonium of the reprocessing campaign.

Although this method is mainly of importance for safeguards purposes, it may be helpful too as a check up for the plant operator himself and for the control of the amounts of processed fuel by the customer. Its application is not restricted to the input accountability of a reprocessing plant but may also be used to determine the contributions of waste streams and final products to the material balance.

In order to receive information on the accuracy which may be expected applying the composite sample technique, the input accountability computed from batchwise analysis has been compared with the values resulting from the analysis of a corresponding composite sample. These investigations have been carried out in connection with the performance of a safeguards experiment at the EUROCHEMIC-Reprocessing Plant in Mol, Belgium [2].

In chapter 2 the principle of the composite sample technique is described in detail and the error formulas for the composite sample technique as well as the single batch analysis method are given. Chapter 3 contains the description of the experimental part. The results obtained are discussed in chapter 4. Finally, in chapter 5 some considerations on the safeguards aspects are given.

2. Principle of the Method

Let M_i be the amount of Pu (resp. U) in the i -th input batch of a reprocessing plant ($i = 1, \dots, n$). The total amount M of Pu in all input batches,

$$M = \sum_{i=1}^n M_i \quad (2.1)$$

is usually obtained by taking a sample of each input batch, determining the Pu-concentration C_i and calculating the total amount M by

$$M = \sum_{i=1}^n C_i V_i \quad (2.2)$$

where V_i is the volume of the i -th input batch.

Note: The following considerations are also valid, if the volumina are replaced by the weights.

The concentration C_i is given by the amount m_i of Pu in the sample divided by the volume v_i of the sample.

Therefore one has from (2.2)

$$M = \sum_{i=1}^n m_i \frac{V_i}{v_i} \quad (2.3)$$

If the ratio V_i/v_i is kept constant for all input batches,

$$\frac{V_i}{v_i} = \frac{1}{\gamma} = \text{const} \quad (2.4)$$

from (2.3)

$$M = \frac{m}{\gamma}; \quad m = \sum_{i=1}^n m_i \quad (2.5)$$

is obtained.

Therefore the Pu-content M of all input batches can be determined by one single analysis, as the Pu-content m of the n samples can be obtained by mixing the n samples together and determining the Pu-concentration C of this 'composite sample'

$$m = C \cdot v; \quad v = \sum_{i=1}^n v_i \quad (2.6)$$

Note: From (2.6) and (2.5) follows

$$M = \frac{C \cdot v}{Y} = C \sum_{i=1}^n \frac{v_i}{Y} = C \sum_{i=1}^n V_i \quad (2.7)$$

Comparing this with (2.2) one obtains

$$C = \frac{\sum_i C_i V_i}{\sum_i V_i} \quad (2.8)$$

Thus, the composite sample technique for determining the Pu content of a campaign consists in determining an averaged weighted concentration and multiplying it by the volume of all input batches.

Now the question raises whether or not the accuracy of the new method destroys the advantage of smaller analytical effort. Therefore for both methods the total errors are calculated and compared. As the basis of the comparison the variance of the concentration is taken as it is given by (2.8). In the case of the single batch analysis method this concentration is calculated from the single C_i 's and V_i 's, in the case of the composite sample technique this concentration is obtained directly as discussed above.

The results of the calculations which are given in annex I are

(i) coefficient of variation in case of the single batch analysis method

$$\delta \bar{C} = \left(\frac{\bar{Y}^2}{n} \delta_{Vr}^2 + \bar{Y}^2 \delta_{Vs}^2 + \frac{\delta_I^2}{nm} + \frac{\delta_{Cr}^2}{nml} + \delta_{Cs}^2 \right)^{\frac{1}{2}} \quad (2.9)$$

(ii) coefficient of variation in case of the composite sample technique

$$\delta C = \left(\frac{\bar{Y}^2}{n} (\delta_{Vr}^2 + \frac{\delta_{vr}^2}{mp}) + \bar{Y}^2 (\delta_{Vs}^2 + \delta_{vs}^2) + \frac{\delta_I^2}{mn} + \frac{\delta_{Cr}^2}{mpl} + \delta_{Cs}^2 \right)^{\frac{1}{2}} \quad (2.10)$$

Here

$$\bar{Y}^2 = \frac{1}{n} \sum_i \left(1 - \frac{EC_i}{EC}\right)^2; \quad \bar{Y}^2 = \left(\frac{1}{n} \sum_i \left(1 - \frac{EC_i}{EC}\right)\right)^2; \quad EC = \bar{EC} \quad (2.11)$$

$$EC = \frac{1}{EV} \sum_i EC_i EV_i; \quad EV = \sum_i EV_i$$

- EC_i, EV_i = true values of C_i and V_i
- δ_{Vr} = coefficient of variation of the error of the single volume measurement (reproducibility)
- δ_{Vs} = coefficient of variation of the volume measurement calibration
- δ_{Cr} = coefficient of variation of the single concentration measurement
- δ_{Cs} = coefficient of variation of the concentration measurement calibration
-
- δ_I = coefficient of variation of the sampling error
- δ_{vr} = coefficient of variation of single aliquotation
- δ_{vs} = coefficient of variation of aliquotation calibration
- n = number of batches
- m = number of samples per batch
- p = number of aliquotations per sample
- l = number of concentration measurements per sample in case of single sample analysis, per composite sample in case of composite sample analysis

Note: In case of single sample analysis it is assumed that the concentration C_i averaged over the $m \cdot l$ analyses per batch is inserted in (2.8). In case of composite sample analysis it is assumed that according to the $m \cdot p$ aliquots per batch $m \cdot p$ composite samples are produced, and that the average over the $m \cdot p \cdot l$ concentration measurement results is taken.

The experimental results presented in this paper indicate that it may be advantageous to dilute the samples immediately after they have been taken in order to reduce the possibility of autoradiolysis during the storage time. Aliquotation for preparing the composite sample is then performed using these diluted sample solutions. In this case, an extension of the method described above becomes necessary. It is given in annex II including the corresponding error considerations.

3. Experimental

3.1 Sampling

From each accountability tank of the reprocessing plant four samples were taken in the usual manner. One sample was used for analysis in the plant operators laboratory (A)¹⁾, two samples for analysis by another laboratory (B)²⁾ and the fourth sample for the preparation of two composite samples I and II.

3 ml glass bottles with rubber stoppers (Fig. 1) were used as sample containers. The samples for laboratory B and for the preparation of the composite samples were stored until shipment after the termination of the reprocessing campaign. The radioactivity of the sample solution was about 150 mCi/ml, the acidity about 2 M in nitric acid. Some of the rubber stoppers were damaged by the nitric acid solution.

The number of dissolutions of the campaign was 14, the total number of batches 30. The standard volumina and density of each batch are summarized in table 1 together with the weight of the solution per batch, calculated from these data. For the total of the campaign, a fuel solution volume of 55.440 l with a weight of 76.256 kg has been found.

3.2 Preparation of the composite samples

3.2.1 Instruments

Besides the standard equipment of the hot cell the following instruments became necessary for the preparation of the composite samples:

5 ml polyethylene one way syringes with stainless hypodermic needles for transferring the sample solution from the stoppered bottles to open containers.

A glass container for collecting and mixing the aliquotes. Its volume was approximately twice the calculated volume of the composite sample. It was equipped with a ground joint of approx. 45 mm upper diameter to allow easy access of the pipetter glass tip. The container could be closed by a teflon stopper with a thermometer capillary, 70 mm long and 0.1 mm diameter. By this means pressure increase in the container by radiolysis could be avoided without any remarkable loss of sample material by convection and evaporation.

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As pipetter, a commercially available motor driven 2 ml burette suitable for remote operation was used with the burette inside and the electronic control unit outside the cell.¹⁾

To avoid cross contamination, the piston of the burette was separated from the sample solution by dodecane as an inert intermediate liquid (Fig. 2). The lower end of the one way tip of the burette was siliconized to guarantee complete stripping of any liquid hanging on. Refilling of intermediate liquid was accomplished by the use of a motor driven three-way-stopcock with limiting switch.

The method of pipetting using throwaway parts and intermediate liquid has been described in the ORNL Analytical Master Manual [6].

3.2.2 Aliquotation

The value of the aliquotation factor

$$\gamma = \frac{\text{volume of the aliquote}}{\text{volume of the fuel solution in the tank}}$$

was chosen in such a way that the size of the largest aliquote remained just below the 2 ml capacity of the pipetter. By this way, the burette volume could be utilized in an optimal manner without the necessity of double pipetting.

The drop of sample liquid usually sticking to the tip after stopping the pipetter was removed in a reproducible way by touching the wall of the sample collection container near the surface at an angle of about 30°. This is done preferably with a drop of relatively large size. It always can be obtained as the last one by stopping the piston of the burette about 3/4 drop volume before the limiting position. After stripping off the drop, movement of the piston is continued until end position. By proceeding in this manner, a reproducibility better than 0.3 % can be obtained.

As it is not possible to push through the rubber cover of the sample bottles with the glass tip of the pipetter, the bottles have to be opened or the sample solution has first to be transferred into another container by use of one way syringes.

Using the same aliquotation factor $\gamma = 4.000 \cdot 10^{-7}$, two composite samples (I and II) were prepared in parallel. This was done in order to preserve at least one

¹⁾ Metrohm, Herisau (Switzerland)

sample in case of a pipetting failure. On the other hand, if no obvious failure was observed, comparison of the analytical results can be considered as a certain proof on the correctness of the sample preparation.

3.3 Analytical procedures and time schedule

The mass spectrometric isotopic dilution method was used for the determination of the U- and Pu-concentrations by laboratory A and B [7,8,9]. In addition, the composite samples were analysed in a third laboratory (C)¹⁾ by X-ray fluorescence-spectrometry [10,11]. Each sample has been prepared separately for analysis including the dilution with nitric acid and the complete spiking procedure for isotopic dilution analysis. For the samples of the input batches, this was done by laboratory B in the mean about one month later than by laboratory A.

At the time the composite samples were prepared, the samples had been stored between 2 and 4 months. Dilution of the composite samples for analysis was carried out about 2 weeks later (Fig. 3).

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4. Results and discussion

4.1 Single batch analysis

The analytical results of the uranium- and plutonium-concentration determinations of each batch are compiled in table 2 for laboratory A and in table 3a and 3b for laboratory B. For the calculation of the U- and Pu-content per batch from these data, the average of the two measurements was used in the case of laboratory B. For a few batches, only rather inaccurate process analytical data or α -spectrometric results were available. Because of the small contribution of these batches to the total campaign, this could be tolerated.

For the mean concentrations \bar{C} of the campaign (i.e. total amount of U and Pu respectively of the campaign divided by the total amount of solution) the following results are obtained:

	Uranium [mg/g solution]	Plutonium [μ g/g solution]
LAB A	163.85	1019.33
LAB B	164.42	1029.13

In order to decide whether or not the differences of the values found by the two laboratories have to be considered as significant, an error calculation according to formula (2.9) was carried out.

The data applied are summarized in table 4. The values of \bar{y}^2 and \bar{z}^2 can be calculated from the analytical results of this experiment, given in tables 2 and 3. For these calculations, the measured values C_i are taken as an approximation for the true values EC_i . Certain assumptions, however, are necessary concerning the values of δ_{Vr} , δ_{Vs} , δ_I , δ_{Cr} and δ_{Cs} .

Based on investigations carried out at the Eurochemic plant [12] a random error for single volume measurement of $\delta_{Vr} = 0.25\%$ and a tank calibration error of $\delta_{Vs} = 0.10\%$ were used as estimates for the coefficients of variation.

The values of 0.2 % and 0.6 % for the random error δ_{Cr} of single analysis for U and Pu respectively, as well as 0.3 % for the analytical calibration error δ_{Cs} are estimations based on the long time experience of the laboratories involved in this experiment [7,9].

Some uncertainty exists in the choice of the most appropriate value for the sampling error δ_I . It is understood to be caused mainly by inhomogeneity of the fuel solution. In normal reprocessing plant operation, density measurements are first carried out on several samples taken from the same batch. Only in case these results agree within certain limits the samples are considered to be representative for the batch. By this way and because of the short time period between sample taking and analysis (see below) the error contribution of δ_I can be kept below 0.4 % ¹⁾. In this experiment however, the samples for laboratory B were not controlled in this manner ²⁾ and they were diluted and spiked for analysis about one month after they had been taken (see Fig. 3). For this reason a higher value for δ_I has to be applied which - besides the possible higher degree of inhomogeneity - takes also into account the random components of changes in the sample composition which may have happened during the time of sample storage ³⁾.

In order to receive the most realistic estimation for δ_I , the mean values $\bar{\delta}_A$ of the relative standard deviations δ_A of all the duplicate analyses performed by laboratory B were calculated for U and Pu (see table 3). As each analytical result represents one single analysis of one individual sample, $\bar{\delta}_A$ is composed of the sampling error δ_I and the random error δ_{Cr} of the analysis itself. Therefore, the relation

$$\bar{\delta}_A^2 = \delta_I^2 + \delta_{Cr}^2$$

can be applied to calculate δ_I . This results in the values of 1.2 % for U and 1.8 % for Pu which are given in table 4 and used for the error calculation.

¹⁾ E.g. from the data given in reference [7] $\bar{\delta}_I = 0.31$ % can be calculated in the case of plutonium.

²⁾ This applies also to the samples taken for the preparation of the composite samples.

³⁾ It should be noted that these are the same conditions as in safeguarding the plant operation if separate samples are taken and sealed for analysis by any control authority.

The value of $\bar{\delta}_A$ and therefore that of δ_I is very much influenced by a rather small number of particular high values of δ_A as it can be seen from the individual figures. In the case of plutonium e.g., suppression of one value only (table 3b, batch 27) would reduce δ_A from 1.9 % to 1.0 % and consequently δ_I from 1.8 % to 0.8 %. However, no justification is seen for rejection of those data if they are understood as caused by inhomogeneity or real changes in the sample composition during the time of storage.

The results of the error calculation are summarized in table 5 showing also the contributions of the different additive terms of formula (2.9) to the total error. It can be seen that in this experiment the main contributions to the total error are given by the analytical calibration error δ_{Cs} and the expression $\delta_I^2/n \cdot m$ which depends to a high degree on the assumption of the sampling error δ_I . The tank calibration error as well as the random errors of volume measurements and analyses have no remarkable influence. Although the values of the different terms depend also on the characteristic of the campaign (total number of batches, concentration differences from batch to batch) and on the analytical efforts (number of samples taken per batch and number of repetition analyses per sample), these statements are valid for a large range of cases.

Fig. 4 shows the mean concentration values for U and Pu calculated from the single batch analyses of the two laboratories with an indication of the error ranges ($\pm 2\%$). The mean concentration values were normalized to those determined by laboratory A. According to the definition of a significant difference given in annex III, the results of the two laboratories have to be considered as not significantly different. However, as the values found by laboratory B for both U and Pu are higher, it has been investigated whether this effect can be explained by different systematic errors in the analytical procedures of laboratory A and B only or whether it may also represent a real increase in concentration caused e.g. by autoradiolysis and hydrolysis during the storage time of the samples analysed by laboratory B.

For this purpose, the ratios of the concentration determinations by the two laboratories A and B for the different batches

$$r_{ij}(C) = \frac{C_{ij}(\text{Lab B})}{C_{i..}(\text{Lab A})}, \quad \begin{array}{l} i = 1 \dots N \\ j = 1 \dots M_i \end{array}$$

and their mean values

$$\bar{r}(C) = \frac{\sum_{i=1}^N \sum_{j=1}^{M_i} r_{ij}(C)}{\sum_{i=1}^N M_i}$$

Were calculated for U and Pu (see table 6).

These two mean values $\bar{r}(C)$ would be the best estimates for the systematic analytical deviations between the two laboratories if these are the only reason for the higher mean concentration values found by laboratory B. They are given in table 7 together with the ratios

$$r(\bar{C}) = \frac{\sum_{i=1}^N V_i C_i \dots (\text{Lab A})}{\sum_{i=1}^N V_i C_i \dots (\text{Lab A})}$$

of the average concentrations calculated from the analyses of the two laboratories A and B according to the single batch method.

A comparison of the values $\bar{r}(C)$ and $r(\bar{C})$ shows, that an explanation of the difference in the results of both laboratories by a systematic analytical deviation only is unsatisfactory. An application of the values $\bar{r}(C)$ as a correction for systematic analytical deviations would reduce the difference of the average concentration values calculated from single batch analyses by 25 % only in the case of Pu and would even increase this difference by 30 % in the case of U.

Although the existence of a systematic analytical deviation between the measurements of the two laboratories can not be excluded by this consideration, the contribution of an additional effect as a real concentration increase for the samples analysed by laboratory B is indicated by these results. If this is caused by autoradiolysis and hydrolysis during the storage time, a dependence of the ratios $r_{ij}(C)$ from the sample concentration C_i and the storage time t could be expected, as these effects should in general become stronger with higher sample concentrations and should increase with time.

In Fig. 5 the values of $r_{ij}(C)$ have been plotted against the product $C_i \cdot t$ (sample concentration \cdot storage time) for the case of Pu. The straight line has been determined by the least square method and the dashed curves limit the

95 % confidence area. The increase of more than 4 % of the ratios $r_{ij}(C)$ within the considered range of $C_{ij} \cdot t$ as given by the regression line confirms the existence of the assumed autoradiolytic effect ¹⁾.

In addition, the coefficients of variation of the $r_{ij}(C)$ values are 3.0 % for Pu and 2.7 % for U. This also indicates that in general the differences from batch to batch are higher than the deviations between the same batch, characterized by the $\bar{\delta}_A$ -values of 1.9 % for Pu and 1.2 % for U calculated before. Taking into consideration that the effect of autoradiolysis is not directly a function of the Pu-concentration but of the qualitative and quantitative sample composition with respect to all radioactive material contained, this higher batch-to-batch variation becomes understandable.

Furthermore, the high number of $r_{ij}(C)$ -values below 1.000²⁾ demonstrates that autoradiolysis and hydrolysis are very probably not the only effects which influence the difference in the results between laboratory A and B. Another effect of opposite sign seems to be superimposed. As the regression line reaches an lowest ordinate value of 0.98 it is indicated that this effect is of the order of 2 %. An explanation by a systematic analytical deviation only seems therefore improbable. At least in addition a real decrease in the concentration of the sample solution e.g. by precipitation or polymerisation has to be assumed. These effects partially compensate an increase in concentration caused by autoradiolysis.

Although by the data obtained in this experiment no final confirmation can be given for the various aging effects on the samples discussed, their existence is strongly indicated and the results are not in contradiction. Besides this, the $r_{ij}(C)$ -values show clearly that differences up to 5 % may occur in the concentration determinations of two samples with an activity of about 150 mCi/ml and a HNO_3 acidity of about 2 M taken from the same batch and analysed by two laboratories with a difference in storage time of about one month.

¹⁾ For U the same behaviour is found on principle, however less pronounced.

²⁾ The ordinate of the centre of gravity S is 1.0003.

4.2 Composite sample analysis

The analytical results on the composite samples I and II obtained by laboratory B (isotopic dilution method) and laboratory C (X-ray fluorescence spectrometry) are summarized in the tables 8a and b. As there exist no significant differences in the values of the two samples determined by each laboratory, the mean values which are also given in the tables have been used for the further considerations.

As already mentioned in 3.2.2, the agreement in the concentration values of the two composite samples can be considered as a certain proof on the accuracy of the sample preparation. Only failures which are identical for both samples would not be indicated.

For the error calculation according to formula (2.10), the data compiled in table 9 were used. The numerical values for the different terms of the expression for the total coefficient of variation are summarized in table 10.

For \bar{y} the mean values of the data found in the error calculation of the single batch method were taken (see table 9). δ_{vs} and δ_{vr} , the calibration error of the pipetter and the random error of pipetting were estimated to be 0.15 % and 0.25 % respectively. This estimation is certainly sufficiently accurate because of the negligible contribution of these parameters to the total error.

The values for the random errors $\delta_{Cr} = 0.6$ % for U and $\delta_{Cr} = 1.0$ % for Pu as well as the calibration error $\delta_{Cs} = 0.3$ % in X-ray fluorescence analysis are based on about 20 comparison analyses performed by laboratory C for testing this analytical technique $\overline{[10]}$.

All the other data correspond to the values used for the error calculation of the single batch method.

Comparison of the contributions of the different additive terms to the total error shows clearly, that in this experiment the influence of all errors in volume determination - on the accountability tank as well as in the aliquotation of the composite sample - is an extremely small one. The total error is nearly exclusively determined by the sampling error and the analytical errors. This statement is to a very far extent independent from the characteristic of the campaign.

Fig. 6 shows the results of the composite sample analyses by laboratory B and C with an indication of the error ranges ($\pm 2\sigma$). The concentration values were again normalized to the values found by laboratory A for single batch analysis. For testing the significance of the differences in the results of both laboratories it is allowed to suppress the first three terms in the expression for the total error, as the samples given to both laboratories were identical. These reduced limits of error are used.

Although the overlapping of the error ranges is rather small, it seems to be most probable that these deviations between the results obtained on the composite samples are caused by analytical errors only. All effects which would influence the values of both elements in the same direction - e.g. change of the sample concentration by evaporation - can be excluded with high credibility because of the opposite sign of the deviation for U compared to that of Pu. Any different aging effects can be excluded to a far extent as the samples have been prepared and analysed by laboratories B and C nearly at the same time (see Fig. 3). The further possible assumption of a characteristic difference in the two analytical methods leading to a higher Pu/U ratio by X-ray fluorescence spectrometry compared to the isotopic dilution mass spectrometry as in this case is also not confirmed by other studies¹⁾.

4.3 Comparison of the single batch method and the composite sample technique

All results obtained by the single batch method and by the analyses of the composite samples are summarized in Fig. 7 with the error ranges calculated before.

All concentration values determined by analyses of the composite samples are higher than those calculated from the single batch analyses of the campaign. If only the results of the isotopic dilution analyses are considered, the difference is about 2.5 % both for U and Pu. The inclusion of X-ray fluorescence analysis decreases the difference to 1.4 % for uranium and increases the difference to 3.1 % for plutonium.

Although there is some overlapping of the error ranges, an explanation of these differences by random errors only is unsatisfactory.

¹⁾ The sign of the systematic deviation given in ref. [10] is positive for U and negative for Pu with respect to the measurements of laboratory B.

As it was shown in Fig. 2 the storage time for the material of the composite samples was about 3.5 times longer than those of the samples used by laboratory B for the single batch analyses. Within the limits of error, this is about the same ratio as that of the differences in the corresponding concentrations especially if the mean values of the composite sample determinations by the laboratories B and C are taken. As an increase in concentration by autoradiolysis and hydrolysis would be at least in first approximation proportional with time, this can be considered as a confirmation that the differences in the concentration values found in this experiment are caused by those effects.

The possibility, that the deviation between the results of the single batch method and the analyses of the composite samples are due to an undetected identical failure in the preparation of the two composite samples I and II can not be excluded on principle but seems very improbable because of the extreme care which was taken in this respect.

An explanation by evaporation of sample solution during the preparation of the composite samples can be excluded. It would necessitate the loss of more than 0.5 ml during this procedure. As the container for collecting the aliquots was only opened during the time necessary for the addition of the aliquots, the possible loss is about one order of magnitude smaller than this amount as it could be shown experimentally.

4.4 Summary and conclusions

In this experiment the results on single batch analysis obtained by a second laboratory about one month after the measurements of the plant operator show an increase of about 1 % for Pu. The concentration determinations on two composite samples carried out by two laboratories about 3.5 months after sampling give a value about 3 % higher than that found by the operator by single batch analyses. For U the values are about one halfth of the corresponding Pu values.

It is strongly indicated, that these concentration differences are mainly caused by autoradiolysis and hydrolysis of the high active samples during the storage time. There is also some evidence, that this concentration increase may be partially compensated by effects of opposite sign like precipitation and/or polymerisation.

As the composite sample technique necessitates always a certain storage time of the sample material a reduction of these aging effects is of principal importance for the application of this method. It may be obtained by dilution of the samples immediately after they have been taken or by the use of techniques which avoid the storage of the sample material in the liquid phase.

Furthermore, special measures should be taken to reduce the possibility of undetected failures in preparing the composite sample to a minimum. In order to control the correct settings of the remote pipetter during aliquotation e.g., the connection of an automatic printing unit would be extremely helpful. Besides this, the amount of composite sample solution prepared should always finally be measured by volume or weight and compared with the computed value. By this way not only gross failures in aliquotation like double pipetting or omission of a sample can be detected but also losses due to evaporation during the procedure.

The detailed error analysis shows that the accuracy obtainable by the single batch method as well as by the composite sample technique depends mainly on the sampling error and the analytical calibration error. The analytical random error is only of importance in the case of a very small number of batches or a small number of repetition measurements of the composite sample. The error contributions of the volumina determinations on the input accountability tank as well as in the aliquotation procedure are negligible. This statement to a far extent seems to be independent of the characteristics of the campaign (number of batches, concentration differences from batch to batch etc.). However, further investigations may become necessary to confirm the validity of the coefficients of variation of the volumina determinations on which the calculations in this paper have been based.

5. Safeguards aspects

5.1 General

In order to determine more clearly the position of the composite sample technique within the different methods which could be used for the control of fissile material in a reprocessing plant, in the following some considerations on the assumptions, advantages and disadvantages of the various techniques are made. Although these considerations are directed to the control of the input of the plant, they are to a certain extent also valid for the control of the product and waste streams.

Two groups of safeguards measures have to be distinguished:

Firstly those which enable the control authority to establish a completely independent material balance,

secondly those which are only thought for verification of the operators data.

It should be noted that sampling and analysis by a completely automatic laboratory connected directly to the input of the reprocessing plant could offer a third possibility in so far as the analytical results obtained could be used by both, the operator and the control authority presuming that such a system can be made tamperresistant. If its function is checked by the control authority from time to time using calibration samples, this method can be considered as somewhere between those for the establishment of an independent material balance and a verification of the operators data only.

It has to be emphasized strongly that two essential assumptions are made for all methods discussed in the following:

1. The volumina and densities of the fuel solution in the input accountability tanks are known to the control authority and cannot be tampered by the plant operator.
2. The sampling procedure is tamperresistant.¹⁾

¹⁾ In practice it is probably impossible to fulfill these two assumptions by the surveillance of an inspector only. The development of appropriate tamperresistant automatic devices may therefore become a necessity.

5.2 Safeguards measures for establishing an independent material balance

For the purpose of establishing an independent material balance both, the single batch analysis method as well as the composite sample technique can be used as described in this paper. According to the results given, in particular the following two assumptions have to be fulfilled to receive a high accuracy:

1. Aging effects of the samples during the storage time until the analyses are performed by the control authority or the composite sample is prepared have to be reduced. Possible ways to accomplish these requirements have already been indicated in par. 4.4 of this paper.
2. Because of the high contribution of the analytical calibration error to the total error of the concentration determination, identical calibration samples should be used by the different laboratories. In practice this involves rather complicated problems concerning the stability of the calibration samples, the possible frequency of their measurement depending on the analytical capacity of the laboratories and the most suitable way of correcting the measurements by the results of such calibration runs.

Both methods, the single batch analysis method as well as the composite sample technique have the disadvantage of a rather long time delay between the sampling procedure and the availability of the results for the control authority.

Whereas in the case of the composite sample technique this difficulty is an inherent property of the method, it is a question of the practicability of fast analyses in the case of the single batch method, in particular if the analyses by the control authority are performed in a laboratory located outside the reprocessing plant ¹⁾.

A comparison of the efforts of the two methods necessary to obtain approximately the same accuracy shows - based on the data of this experiment and using the error formular (2.10) - a clear advantage of the composite sample technique. In table 11 the effort of the single batch analysis method is compared with two different kinds of application of the composite sample technique, all resulting in approximately the same accuracy ²⁾.

¹⁾ From this point of view, the use of an automatic analytical laboratory installed at the reprocessing plant would be of advantage. Such a laboratory would also offer the possibility of frequent calibration runs because of its high sample throughput.

²⁾ For these considerations the data for Pu have been used.

In case of the composite sample technique "I", it has been assumed that one sample is taken from each batch and that one composite sample has been prepared from these samples. As it can be seen from the data given in the table, 10 analyses of the composite sample are necessary to obtain approximately the same accuracy as by the analysis of 30 samples according to the single sample batch method ¹⁾. The additional effort of composing one sample is with certainty very small compared to that of 20 analyses which can be saved.

A further reduction of the number of analyses is obtained by the composite sample technique "II" (see also table 11). In this case it is assumed, that 4 samples are taken per batch and that from each of these four sets of samples one composite sample is prepared and only once analysed. This results also in an error of 0.46 % because of the reduction of the term $\delta_I^2/n m$ in the error formula (2.10). Although the advantage of a reduction of the number of analyses from 10 to 4 in comparison to the composite sample technique "I" has to be confronted with the higher investments in sampling and composite sample preparation, the total effort may still be smaller, especially if the expensive mass spectrometric isotopic dilution method has to be used for analysis. The appropriate choice between these two kinds of the composite sample technique depends to a far extent on the magnitude of the sampling error which has to be expected in the special application.

However, there exists a principal difference in these two types of application of the composite sample technique which should be taken into consideration in establishing the most suitable safeguards measures: If the composite sample technique "I" is used and if it can be guaranteed by any means that material of the identical sample ²⁾ is used for analysis by the plant operator as well as the control authority ³⁾, the term $\delta_I^2/n m$ can be suppressed in the error formulas (2.9) and (2.10) respectively if only the comparison of the results on the concentration determinations obtained by the plant operator and the

1) A comparison of the error formular (2.9) and (2.10) shows that by the composite sample technique "I" and the single batch analysis method exactly the same accuracy can only be achieved if the number of analyses is equal. In this example this would mean that an increase of the number of repetition measurements of the composite sample by a factor of 3 (from 10 to 30) is necessary to obtain the nearly negligible error reduction from 0.48 % to 0.46 %.

2) If the sample is diluted immediately after it has been taken in order to reduce aging effects, sample material of the same dilution has to be taken respectively.

3) In practice, this may become very difficult in particular if the control is performed by the surveillance of an inspector and not by an automatic tamperresistant device.

control authority is of interest. This leads to a reduction of the error ranges and thereby to more distinct statements on the significance of eventual deviations¹⁾. The use of identical sample material by the plant operator and the control authority is of course only a possibility but not a necessity for the application of the composite sample technique "I".

In the case of the composite sample technique "II" this possibility principally does not exist as various samples per batch are used. However, the concentration value determined will represent the true concentration to a higher approximation because of the averaging over sampling errors.

As it has been shown, the analytical efforts necessary for both kinds of the composite sample technique are remarkably lower than for the single batch analysis method. As the number of analyses can be considered as the determining parameter, the relative savings by use of the composite sample technique increase with the number of batches of the campaign which are covered.

Depending on the information needed for a finally established safeguards system it may be an disadvantage of the composite sample technique that no detailed data on the concentrations and the isotopic compositions of the single batches are obtained, as in the case of the single batch analysis method. As far as the isotopic compositions are concerned, there exist two possibilities to overcome this difficulty at least partially:

Firstly, the comparison of the isotopic composition measured on the composite sample with the mean isotopic composition calculated from the single batch data of the plant operator. This verification method, which is discussed later in more detail, gives at least a limited proof on the correctness of the information.

Secondly, the advantage of the composite sample technique compared to the single batch analysis method remains - however to a smaller degree - even if relative isotopic abundance determinations on the single batch samples are performed. Especially this is the case if e.g. for the application of the

¹⁾ It has to be realized, however, that the use of identical sample material by the plant operator and the control authority reduces the independence of the material balance established by the control authority and leads to a certain extent towards the principle of verification.

minor isotopes safeguards technique (MIST) or the observation of step functions the number of batches of a campaign which has to be analysed in respect to the isotopic composition can be limited.

5.3 Safeguards measures for verification purposes

If only the verification of the plant operators data but not the establishment of an independent material balance shall be performed by the control authority, different modifications of the single batch analysis method and the composite sample technique are possible. As the basic methods have already been discussed before and because of the impossibility to study their effectivity in detail without treating the complex problem of optimisation of the safeguards measures on the complete fuel cycle¹⁾, only some fundamental features of these methods are discussed briefly in the following.

5.3.1 Single batch analysis method using randomly selected batches

Verification of the operators data by the analysis of samples taken randomly from single batches of a campaign is the probably most often used method until now.

The basic problems of this method are very similar to those of the single batch analysis method for establishing a complete independent material balance. According to the results given in this paper, deviations of a few percent between the concentration determinations by the plant operator and the control authority may occur if aging effects on the samples are involved (see page 14).

If the mass spectrometric isotopic dilution method is used for the concentration determinations, the effectivity of this type of verification measure is strongly influenced in a unfavorable manner by the high costs of this analytical technique. If however only the operators data on the relative isotopic abundances shall be verified, this method of analysis on samples of randomly selected single batches is the most suitable one.²⁾

1) The optimisation of the variance of the input stream of a reprocessing plant is only meaningful in connection with the optimisation of the variance of the complete fuel cycle.

2) Contrary to the verification of the relative isotopic abundances using the composite sample technique as described later in par. 5.3.2, it is independent of any concentration determinations of the element, aging effects of the sample and the batch-to-batch variances of the relative isotopic abundances.

5.3.2 Composite sample technique using randomly selected batches

This method corresponds completely to the composite sample technique as used for the establishment of an independent material balance with the only difference that for the aliquotation only samples of randomly selected batches are used. Besides the for verification purposes rather unimportant disadvantage that the detailed information on the single batches chosen is lost, the effectivity of this method can be expected to be considerably higher than in the case of the single sample analysis of randomly selected batches for the same reasons as discussed in par. 5.2.

The development of the safeguards system may lead to the conclusion that it is advantageous to take samples for the control authority principally on each batch and to select from this complete set of samples afterwards randomly those for the preparation of the composite sample. In this case the question has to be raised, whether it is still meaningful to use only a part of these samples randomly selected for the preparation of the composite sample. The savings compared to the application of the composite sample technique using all samples which allows the establishment of an independent material balance are only the smaller number of aliquotations necessary, whereas the sampling and analytical efforts are the same.

If there are relatively high differences of the relative isotopic abundances from batch to batch, this composite sample technique using samples of randomly selected batches for verification purposes may be simplified by measurement of the isotopic ratios of the composite sample only (instead of a concentration determination) and comparison of these results with the isotopic ratios calculated from the operators data. As the ratio of two isotopes x and y of the composite sample is given by

$$R_{x,y} = \frac{\sum_i C_{xi} V_i}{\sum_i C_{yi} V_i} = \frac{\sum_i R_{xyi} C_{yi} V_i}{\sum_i C_{yi} V_i} ; R_{xyi} = \frac{C_{xi}}{C_{yi}}$$

(V_i volume of the ith batch, $C_{x(y)i}$ concentration of isotope x(y) of the ith batch)

this method of verification applies to the data of the isotopic abundances as well as the concentrations reported by the plant operator simultaneously in a complex correlation. Although the advantage of the high precision obtainable

in the determination of isotopic ratios by mass spectrometry is reduced due to the dependence of the calculated value of R on the less accurately measured concentrations, this method is of principal interest because of the small efforts necessary and the fact that the possibility of verification on the ratios of different isotopes leads to a high degree of tamperresistance. The range of its meaningful application should therefore be studied in more detail.

A further remarkable feature in the application of the composite sample technique for verification purposes only is the fact that there is no necessity for the use of a constant aliquotation factor in preparing the composite sample as in the case of its application for establishing an independent material balance.

Based on the plant operators data for the Pu(U)-concentrations C_i of the single batches the concentration of the composite sample can be calculated according to

$$C = \frac{\sum_i C_i \gamma_i V_i}{\sum_i \gamma_i V_i} ; \gamma_i = \frac{v_i}{V_i}$$

where v_i is the sample volume and V_i is the batch volume.

The value of γ_i can be chosen by the control authority for the aliquote of each sample in a different and for the plant operator unknown way.

The corresponding expression in case of the use of the isotopic ratio method described above is

$$R_{x,y} = \frac{\sum_i C_{xi} \gamma_i V_i}{\sum_i \gamma_i V_i} = \frac{\sum_i R_{xyi} C_{yi} \gamma_i V_i}{\sum_i \gamma_i V_i}$$

This special feature of this method offers two advantages:

Firstly, the preparation of the composite sample is simplified and needs less instrumental equipment as it is sufficient to know the exact value of the aliquote taken, whereas it is not necessary that it has a special predetermined value.

Secondly the verification of the operators data can be optimised by suitable choice of the aliquotation factors in dependence of the concentration and amounts of the corresponding batches.

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ANNEX IDerivation of error formulas

- (1) Derivation of the error of the composite sample concentration calculated from single batch analysis results.

Let be C_{ijk} the k -th repeated concentration measurement ($k=1, \dots, l$) of the j -th sample ($j=1, \dots, m$) of the i -th batch ($i=1, \dots, n$). Let be

$$C_{ij.} = \frac{1}{l} \left(\sum_k C_{ijk} \right); C_{i..} = \frac{1}{m} \sum_j C_{ij.} = \frac{1}{ml} \sum_{jk} C_{ijk} \quad (A1)$$

Then according to (2.0) the composite sample concentration is given by

$$\bar{C} = \frac{\sum_i C_{i..} V_i}{\sum_i V_i} \quad (A2)$$

C_{ijh} and V_i are random variables because of random measurement errors and inhomogeneities of the concentration in the batches. Let be

$$V_i = EV_i + a_i; a_i = a_i' + a \quad (A3)$$

$$\text{var } a_i = \text{var } a_i' + \text{var } a = \sigma_{V_i, r}^2 + \sigma_{Vs}^2$$

Here, EV_i is the expectation value of V_i , a_i is the measurement error, which consists of the error of the single measurement a_i' (reproducibility) and the calibration error a ('systematic error').

Note: The random variables a_i and a_j are not independent. From (A3) one obtains

$$\text{cov}(a_i, a_j) = \sigma_{Vs}^2 \quad \text{for } i \neq j$$

Furthermore, let be

$$C_{ijk} = EC_i + c_{ijk}$$

$$C_{ijk} = d_{ij} + b_{ijk}; b_{ijk} = b_{ijk}' + b \quad (A4)$$

Here, EC_i is the concentration in the i -th batch, d_{ij} the deviation of the true concentration in the j -th sample of the i -th batch from the true concentration in the i -th batch, b_{ijk} the measurement error

(reproducibility b_{ijk}' and calibration error b).

The variances of these random variables are given by

$$\text{var } d_{ij} = \sigma_I^2 ; \text{var } b_{ijk} = \sigma_{C_i r}^2 + \sigma_{Cs} \quad (A5)$$

From (A1) one obtains with (A4)

$$C_{i..} = EC_i + c_{i..} = EC_i + d_{i.} + b_{i..}' + b \quad (A6)$$

The variances of $d_{i.}$ and $b_{i..}'$ are given by

$$\text{var } d_{i.} = \frac{\sigma_I^2}{m} ; \text{var } b_{i..}' = \frac{\sigma_{C_i r}^2}{ml} \quad (A7)$$

From (A2) one obtains with (A4)

$$\bar{C} = \frac{\sum_i (EC_i + c_{i..})(EV_i + a_i)}{\sum_i (EV_i + a_i)}$$

Assuming that the errors are small compared to the expectation values one obtains

$$\bar{C} = EC + \frac{1}{E^2 V} \sum_i (a_i' + a)(EC_i - EC) + d_{i.} EV_i + b_{i..}' EV_i + b$$

Here, EC and EV are given by

$$EV = \sum_i EV_i ; EC = \frac{\sum_i EC_i EV_i}{\sum_i EV_i} \quad (A8)$$

EC is up to terms of higher order the expectation value of C . The variance of \bar{C} is given by

$$\text{var } \bar{C} = \frac{1}{E^2 V} \sum_i \sigma_{V_i r}^2 (EC_i - EC)^2 + \sigma_{Vs}^2 \left(\sum_i (EC_i - EC)^2 + \sum_i \left(\frac{\sigma_I^2}{m} + \frac{\sigma_{C_i r}^2}{ml} \right) E^2 V_i + \sigma_{Cs}^2 \right)$$

If one assumes that all the volumes are approximately the same, and

if one introduces the coefficients of variation $\delta C = \sigma C / EC$ etc., one obtains with

$$\frac{1}{n} \sum_i \left(1 - \frac{EC_i}{EC}\right)^2 = \bar{\gamma}^2 ; \left(\frac{1}{n} \sum_i \left(1 - \frac{EC_i}{EC}\right)\right)^2 = \bar{\gamma}^2 \quad (A9)$$

the result

$$\delta^2 \bar{C} = \frac{\bar{\gamma}^2}{n} \delta^2_{Vr} + \bar{\gamma}^2 \delta^2_{Vs} + \frac{\delta^2_I}{nm} + \frac{\delta^2_{Cr}}{nml} + \delta^2_{Cs} \quad (A10)$$

- (2) Derivation of the error of the composite sample concentration obtained from the composite sample technique.

It is assumed that from each of the n batches m samples are taken and that from each sample p aliquots are taken. This results in $m \cdot p$ composite samples each of which is analysed l times. As the result of the measurement the average value of the $m \cdot p \cdot l$ single analyses is taken.

In the following firstly the case of n batches, $m=p=l=1$ is considered.

The determination of the composite sample concentration with the help of the composite sample technique consists of the following three steps:

First step: Measurement of the batch volumina V_1, \dots, V_n . As above (A3)

$$V_i = EV_i + a_i ; a_i = a'_i + a \quad (A11)$$

Second step: Aliquotation of sample volumina v_i . According to (2.4) one wants to have the volume $\gamma \hat{V}_i$, where \hat{V}_i is a special realisation of V_i . If one defines v_i as the total experiment 'measurement' of the batch volume and aliquotation of the sample volume, one has

$$v_i = \gamma V_i + l_i = \gamma(EV_i + a_i) + l_i = l'_i + l \quad (A12)$$

Here, l_i is the error of the aliquotation of v_i (random l'_i and systematic l). If one assumes that the measurement errors a_i and l_i are independent, one has

$$EV_i = \gamma EV_i ; \text{var } v_i = \text{var } l_i + \gamma^2 \text{var } a_i \quad (A13)$$

Here, $\text{var } l_i$ is the variance of l_i , it is given by

$$\text{var } l_i = \text{var } l_i' + \text{var } l = \sigma_{v_i, r}^2 + \sigma_{v_i, s}^2 \quad (\text{A14})$$

Third step: Analysis of the concentration of the composite sample. The volume of the composite sample is given by

$$v = \sum_i v_i \quad (\text{A15})$$

If as above EC_i is the true concentration of the i -th batch and there exist no inhomogeneities (that means the true concentration of the sample is equal to the true concentration of the batch), the true concentration of the composite sample is given by

$$EC = \frac{1}{v} \sum_i EC_i \cdot v_i \quad (\text{A16})$$

If d_i is the difference between the true concentration of the i -th batch and the true concentration of the sample, the true concentration of the composite sample is given by

$$EC = \frac{1}{v} \sum_i (EC_i + d_i) v_i \quad (\text{A17})$$

The measured composite concentration is given by

$$C = \frac{1}{v} \sum_i (EC_i + d_i) v_i + c; \quad c = c' + c'' \quad (\text{A18})$$

Here, c is the concentration measurement error (reproducibility c' and calibration error c'').

From (A18) one obtains with (A12)

$$C = \frac{\sum_i (EC_i + d_i) (1_i + \gamma(EV_i + a_i))}{\sum_i (1_i + \gamma(EV_i + a_i))} + c \quad (\text{A19})$$

Assuming again that the errors are small compared to the true values, one obtains with (A8)

$$\frac{C}{EC} = 1 + \frac{1}{EV} \sum_i \left[\left(\frac{l_i'}{\gamma} + \frac{1}{\gamma} + a_i' + a \right) \left(1 - \frac{EC_i}{EC} \right) + d_i \frac{EV_i}{v} \right] + c$$

Assuming again, that the volumes are approximately the same, one obtains with (A9)

$$\delta^2 C = \frac{\bar{\sum}^2}{n} (\delta_{Vr}^2 + \delta_{vr}^2) + \bar{\sum}^2 (\delta_{Vs}^2 + \delta_{vs}^2) + \frac{\delta_I^2}{n} + \delta_{cr}^2 + \delta_{cs}^2 \quad (A20)$$

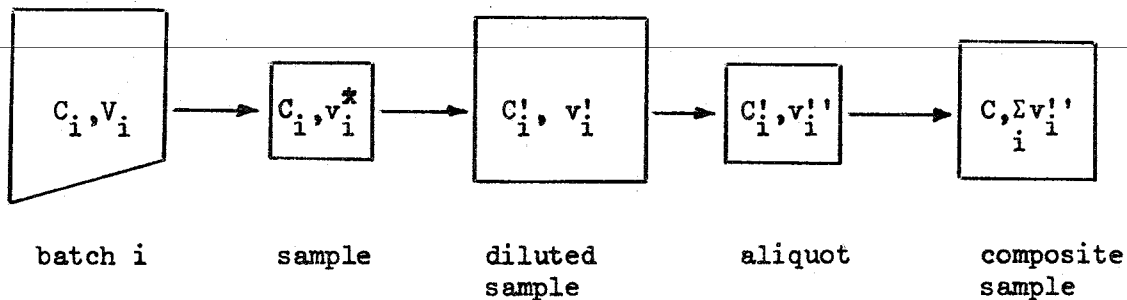
In case of m samples per batch, p aliquots per sample and l analyses per composite sample this expression transforms to

$$\delta^2 C = \frac{\bar{\sum}^2}{n} (\delta_{Vr}^2 + \frac{\delta_{vr}^2}{mp}) + \bar{\sum}^2 (\delta_{Vs}^2 + \delta_{vs}^2) + \frac{\delta_I^2}{nm} + \frac{\delta_{cr}^2}{mpl} + \delta_{cs}^2$$

(A21)

ANNEX IIComposite sample technique with intermediate dilution step

As mentioned in chapter 2, it may be advantageous, not to take the aliquot $v_i = \gamma V_i$ directly from the sample of the batch i , but firstly to dilute the sample volume v_i^* (~ 1 ml) to a volume v_i' (~ 250 ml) and to take the aliquot v_i'' from the diluted sample v_i' .



According to (2.3,5) for the 'direct aliquot' v_i one has

$$M = \sum_i C_i V_i = \sum_i C_i \gamma v_i = \gamma \sum_i C_i v_i = \gamma m \quad (\text{A22})$$

where C_i is the concentration in the i -th batch and γ is the ratio of v_i and V_i given before (2.4). Let be

$$v_i = \alpha_i v_i^* = \gamma \cdot V_i \quad (\text{A23})$$

and furthermore

$$v_i' = \frac{v_i^*}{\lambda_i} \quad (\text{A24})$$

Then the concentration C_i' in the diluted sample is given by

$$C_i' = \frac{C_i}{\lambda_i} \quad (\text{A25})$$

In order to maintain the relation (A22) one has to determine v_i'' in such a way that

$$C_i v_i = C_i' v_i'' \quad (\text{A26})$$

From this relation one obtains with (A 23,25)

$$v_i^{!'} = \gamma \cdot \lambda_i \cdot V_i = \gamma \cdot \frac{v_i^*}{v_i^!} \cdot V_i \quad (\text{A27})$$

Therefore the modified composite sample technique consists of the following four steps:

- (1) From the i -th batch with volume V_i a sample of volume v_i^* is taken.
- (2) The volume v_i^* is diluted to the volume $v_i^!$.
- (3) From the diluted sample an aliquot of volume $v_i^{!'}$ (A27) is taken.
- (4) The aliquots $v_i^{!'}$ are put together and analysed.

In order to determine the error of this method of determining the concentration of the composite sample, the same steps as in Annex I are considered.

First step: Measurement of the batch volumina V_i, \dots, V_n .

As in (A3)

$$V_i = EV_i + a_i ; a_i = a_i^! + a$$

Second step: Aliquotation of the sample volumina $v_i^{!'}$.

According to (A27) one wants to have the volume $\gamma(v_i^* \cdot V_i / \hat{v}_i^!)$, where $(v_i^* \cdot V_i / \hat{v}_i^!)$ is a special realisation of $v_i^* \cdot V_i / v_i^!$. If one defines $v_i^{!'}$ as the total experiment' measurement of V_i + measurement of v_i + measurement of $v_i^!$ + aliquotation' one has instead of (A12)

$$\begin{aligned} v_i^{!' } &= \gamma \frac{v_i^* \cdot V_i}{v_i^!} + l_i = \frac{(Ev_i^* + b_i)(EV_i + a_i)}{(Ev_i^! + f_i)} + l_i = \\ &= Ev_i^{!' } + \gamma \left(\frac{Ev_i^*}{Ev_i^!} \cdot a_i + \frac{EV_i}{Ev_i^!} b_i - \frac{E_i}{Ev_i^!} f_i \right) + l_i \end{aligned} \quad (\text{A28})$$

Here, $Ev_i^{!'}$ is defined as $\gamma Ev_i^* EV_i / Ev_i^!$; $b_i = b_i^! + b$ is the error of the measurement of v_i^* and $f_i = f_i^! + f$ is the error of the measurement of $v_i^!$.

Third step: Analysis of the concentration of the composite sample. According to (A18) the measured composite sample concentration is given by

$$C = \frac{1}{v''} \sum_i (EC_i + d_i) v_i'' + c ; v'' = \sum_i v_i''$$

This gives with (A29)

$$C = \frac{\sum_i (EC_i + d_i) \left[Ev_i'' + \gamma \left(\frac{Ev_i^*}{Ev_i'} \cdot a_i + \frac{Ev_i}{Ev_i'} b_i - \frac{1}{\gamma} \frac{Ev_i''}{Ev_i'} \cdot f_i \right) + l_i \right]}{\sum_i \left[Ev_i'' + \gamma \left(\frac{Ev_i^*}{Ev_i'} \cdot a_i + \frac{Ev_i}{Ev_i'} b_i - \frac{1}{\gamma} \frac{Ev_i''}{Ev_i'} \cdot f_i \right) + l_i \right]} + c$$

Expansion of this expression gives with (A8)

(A29)

$$\frac{C}{EC} = 1 + \frac{\gamma}{Ev_i''} \sum_i \left[\left(\frac{EC_i}{EC} - 1 \right) \left(\frac{Ev_i^*}{Ev_i'} a_i + \frac{Ev_i}{Ev_i'} b_i - \frac{1}{\gamma} \frac{Ev_i''}{Ev_i'} f_i + \frac{l_i}{\gamma} \right) + \frac{Ev_i''}{\gamma} d_i \right] + c$$

With the assumption that all volumes are about the same, the variance of this expression is given by

$$\begin{aligned} \delta^2 C &= \frac{\gamma^2}{n} (\delta_{Vr}^2 + \delta_{v_r^*}^2 + \delta_{v_r'}^2 + \delta_{v_r''}^2) + \\ &+ \frac{\gamma^2}{n} (\delta_{Vs}^2 + \delta_{v_s^*}^2 + \delta_{v_s'}^2 + \delta_{v_s''}^2) + \frac{\delta_I^2}{n} + \delta_{Cr}^2 + \delta_{Cs}^2 \end{aligned} \quad (A30)$$

In case of m samples per batch, p aliquots per sample and l analyses per composite sample one obtains from (A30)

$$\begin{aligned} \delta^2 C &= \frac{\gamma^2}{n} (\delta_{Vr}^2 + \frac{\delta_{v_r^*}^2}{m} + \frac{\delta_{v_r'}^2}{m} + \frac{\delta_{v_r''}^2}{m \cdot p}) + \\ &+ \frac{\gamma^2}{n} (\delta_{Vs}^2 + \delta_{v_s^*}^2 + \delta_{v_s'}^2 + \delta_{v_s''}^2) + \frac{\delta_I^2}{n \cdot m} + \frac{\delta_{Cr}}{mpl} + \delta_{Cs}^2 \end{aligned}$$

(A31)

ANNEX IIIAnalysis of systematic errors

In order to decide if there exist systematic differences between the calculated and the measured composite sample concentration C_I respectively C_{II} , one can perform the following test [13]

$$\begin{array}{ll} C_I - C_{II} < d & \text{no systematic errors} \\ \text{If} & \text{then} \\ & \text{(A32)} \end{array}$$

$$C_I - C_{II} > d \quad \text{systematic errors}$$

The boundary d of the critical region is determined by the error first kind α given in advance:

$$1 - \alpha = \phi\left(\frac{d}{\sigma}\right); \quad \sigma^2 = \sigma_I^2 + \sigma_{II}^2 \quad \text{(A33)}$$

(e.g. from $\alpha = 0.05$ one obtains $d \sim 2\sigma$).

Here, σ_I^2 and σ_{II}^2 are the variances given by (A34) and (A21), multiplied by $E^2 C$.

Note: Relation (A33) holds only if the random variables are normal distributed. This is assumed here.

According to the construction of the test two possibilities exist:

(1) The result of the test is 'no systematic errors exist'.

In this case both concentrations can be taken as estimate for the true composite sample. One also can take a minimum variance estimate in form of a weighted average of both concentrations [14].

(2) The result of the test is 'systematic errors exist'.

In this case one wants to have an estimate for the systematic error. An unbiased estimate for the difference of the two systematic errors of both concentration determinations (single and composite) is given by $C_I - C_{II}$. This estimate may have a large variance, therefore, according to (A32) as 'significant systematic error' (or 'significant difference') the difference

$$C_I - C_{II} - 2\sigma; \sigma^2 = \sigma_I^2 + \sigma_{II}^2 \quad (A35)$$

is defined. This quantity may also be interpreted as a lower limit for the difference between the two systematic errors.

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TABLE 1 Data of the Campaign

Batch No.	Standard volume [l]	Density [kg/l]	Fuel Solution [kg]
1	2462.7	1.5243	3753.9
2	1033.8	1.2445	1286.6
3	2491.9	1.504	3747.8
4	1010.9	1.317	1331.4
5	2632.5	1.4928	3929.8
6	985.6	1.245	1227.1
7	2535.6	1.4835	3761.6
8	983.2	1.282	1260.5
9	2394.6	1.4973	3585.4
10	1495.3	1.2373	1850.1
11	2565.5	1.5185	3895.7
12	1415.6	1.164	1647.8
13	1944.5	1.014	1971.7
14	2361.5	1.4995	3541.1
15	1190.1	1.3045	1552.5
16	2119.9	1.4878	3154.0
17	1652.4	1.2640	2088.6
18	1684.2	1.0140	1707.8
19	2726.4	1.4098	3843.7
20	2508.1	1.4988	3759.1
21	1229.9	1.2225	1503.6
22	2431.2	1.5185	3691.8
23	1393.6	1.168	1627.7
24	2867.0	1.5448	4428.9
25	572.5	1.0267	587.8
26	2695.0	1.5723	4237.3
27	442.2	1.0139	448.3
28	2773.1	1.3758	3815.2
29	1753.9	1.0176	1784.8
30	1087.3	1.1352	1234.3
Total	55440.0		76255.9

TABLE 2 Data of Single Batch Analysis Method for Laboratory A

Batch No.	Uranium				Plutonium			
	Concentration $C_{i..}$ [mgU/g solution]	Uranium per batch [kg]	$1 - \frac{C_{i..}}{\bar{C}}$	$(1 - \frac{C_{i..}}{\bar{C}})^2$	Concentration $C_{i..}$ [μgPu/g solution]	Plutonium per batch [g]	$1 - \frac{C_{i..}}{\bar{C}}$	$(1 - \frac{C_{i..}}{\bar{C}})^2$
1	194.9	731.64	-0.1895	0.0359	1283.2	4817.00	-0.2589	0.0670
2	114.3	147.06	0.3024	0.0914	716.9	922.36	0.2967	0.0880
3	196.7	737.19	-0.2005	0.0402	1192.8	4470.38	-0.1702	0.0290
4	145.9	194.25	0.1096	0.0120	905.1	1205.05	0.1121	0.0126
5	198.2	778.89	-0.2096	0.0439	1194.9	4695.72	-0.1722	0.0297
6	125.7	154.25	0.2328	0.0542	771.2	946.34	0.2434	0.0592
7	200.2	753.07	-0.2218	0.0492	1234.9	4645.20	-0.2115	0.0447
8	133.9	168.78	0.1828	0.0334	851.0	1072.69	0.1651	0.0273
9	198.6	712.06	-0.2121	0.0450	1234.7	4426.89	-0.2113	0.0446
10	116.0	214.61	0.2920	0.0853	712.7	1318.57	0.3003	0.0905
11	199.1	775.63	-0.2151	0.0463	1346.7	5246.34	-0.3212	0.1032
12	84.0 ¹⁾	138.42	0.4873	0.2375	560.6 ²⁾	923.76	0.4500	0.2025
13	0.6 ¹⁾	1.18	0.9963	0.9926	3.2 ²⁾	6.31	0.9969	0.9938
14	205.9	729.11	-0.2566	0.0658	1251.8	4432.75	-0.2281	0.0520
15	137.3	213.93	0.1590	0.0253	841.7	1306.74	0.1743	0.0304
16	217.1	684.73	-0.3250	0.1056	1349.0	4254.75	-0.3234	0.1046
17	133.2 ¹⁾	278.20	0.1871	0.0350	834.7 ²⁾	1743.35	0.1811	0.0328
18	0.9 ¹⁾	1.54	0.9945	0.9890	9.2 ²⁾	15.71	0.9910	0.9821
19	165.6	636.52	-0.0107	0.0001	1091.6	4195.78	-0.0709	0.0050
20	203.2	763.85	-0.2402	0.0577	1193.0	4484.61	-0.1704	0.0290
21	118.0	177.42	0.2798	0.0783	696.4	1047.11	0.3168	0.1004
22	212.3	783.77	-0.2957	0.0874	1201.8	4436.81	-0.1790	0.0320
23	88.2	143.56	0.4617	0.2132	493.9	803.92	0.5155	0.2657
24	218.2 ¹⁾	966.39	-0.3317	0.1100	1403.4 ²⁾	6215.52	-0.3768	0.1420
25	14.1 ¹⁾	8.29	0.9139	0.8352	124.7 ²⁾	73.30	0.8777	0.7704
26	218.9 ¹⁾	927.54	-0.3360	0.1129	1403.0 ²⁾	5944.93	-0.3764	0.1417
27	4.6 ¹⁾	2.06	0.9719	0.9446	31.6 ²⁾	14.17	0.9690	0.9390
28	160.8 ¹⁾	613.48	0.0186	0.0003	1062.7 ²⁾	4054.41	-0.0425	0.0018
29	0.6 ¹⁾	1.07	0.9963	0.9926	3.5 ²⁾	6.25	0.9966	0.9932
30	45.4	56.04	0.7229	0.5226	2.9	3.58	0.9972	0.9944
Total		12494.53	+5.2644	6.9425		77730.30	+5.4709	7.4086
3)		163.85 [mgU/g solution]				1019.33 [μg Pu/g solution]		

1) Rough process analyses data.
2) Measured by α-spectrometry

3) $\bar{C} = \frac{\text{total amount of U(Pu) of the campaign}}{\text{total amount of fuel solution}}$

Table 3a

Data of Single Batch Analysis Method for Laboratory B

URANIUM

Batch No.	Sample age t [days]	1. Concentration determination C_{i1} . [mg U/g solution] ¹⁾	2. Concentration determination C_{i2} . [mg U/g solution] ¹⁾	Mean Concentration value $C_{i..}$ [mg U/g solution]	Relative standard deviation δ_A [%]	Uranium per batch [kg]	$1 - \frac{C_{i..}}{\bar{C}}$	$(1 - \frac{C_{i..}}{\bar{C}})^2$
1	36	200.94	186.48	193.71	5.3	727.17	-0,1781	0,0317
2	36	111.86	112.54	112.20	0.4	144.36	0,3176	0,1009
3	33	191.74	190.32	191.03	0.5	715.94	-0,1618	0,0262
4	33	139.84	141.02	140.43	0.6	186.97	0,1459	0,0213
5	30	194.27	192.83	193.55	0.5	760.61	-0,1772	0,0314
6	30	117.09	117.22	117.16	0.1	143.77	0,2874	0,0826
7	31	217.48	205.32	211.40	4.1	795.20	-0,2857	0,0816
8	31	137.45	135.47	136.46	1.0	172.01	0,1701	0,0289
9	33	202.40	202.91	202.66	0.2	726.62	-0,2326	0,0541
10	33	116.78	116.79	116.79	0.0	216.07	0,2897	0,0839
11	22	203.85	200.26	202.06	1.3	787.17	-0,2289	0,0524
12	22	84.88 ²⁾	84.99	84.94	0.1	139.96	0,4834	0,2337
13	—	0.6 ²⁾	—	0.6	—	1.18	0,9964	0,9928
14	19	204.50	201.29	202.90	1.1	718.49	-0,2340	0,0548
15	19	140.17	140.65	140.41	0.2	217.99	0,1460	0,0213
16	15	214.98	215.88	215.43	0.3	679.47	-0,3102	0,0962
17	15	132.32	130.51	131.42	1.0	274.48	0,2007	0,0403
18	41	0.89	0.98	0.94	6.7	1.61	0,9943	0,9886
19	39	166.24	165.62	165.93	0.3	637.79	-0,0092	0,0001
20	36	206.12	203.72	204.92	0.8	770.31	-0,2463	0,0607
21	36	116.16	117.48	116.82	0.8	175.65	0,2895	0,0838
22	33	215.21	215.66	215.44	0.1	795.36	-0,3103	0,0963
23	33	87.80	88.09	87.95	0.2	143.16	0,4651	0,2163
24	31	221.79	—	221.79	—	982.29	-0,3489	0,1217
25	31	14.09	14.39	14.24	1.5	8.37	0,9134	0,8343
26	29	219.75	222.03	220.89	0.7	935.98	-0,3434	0,1179
27	29	5.05	5.04	5.05	0.1	2.26	0,9693	0,9395
28	26	164.36	161.13	162.75	1.4	620.92	-0,0102	0,0001
29	26	0.62 ²⁾	0.59	0.61	3.6	1.09	0,9963	0,9926
30	—	45.4 ²⁾	—	45.4	—	56.04	0,7239	0,5240
Total					32.9 (27 δ_A)	12538.29	+5,3326	7,0100

1) The 1. and 2. concentration determination were performed on different samples.

2) As not measured by laboratory B, the value of laboratory A has been taken.

$$\bar{C} = \frac{\text{Total amount of U of the campaign}}{\text{Total amount of fuel solution}} = 164.42 \text{ [mg U/g solution]}$$

Table 3b

Data of Single Batch Analysis Method for Laboratory B

P L U T O N I U M

Batch No.	Sample age t [days]	1. Concentration determination C_{i1} [$\mu\text{g Pu/g solution}$]	2. Concentration determination C_{i2} [$\mu\text{g Pu/g solution}$]	Mean Concentration value $C_{i..}$ [$\mu\text{g Pu/g solution}$]	Relative standard deviation δ_A [%]	Plutonium per batch [μg]	$1 - \frac{C_{i..}}{\bar{C}}$	$(1 - \frac{C_{i..}}{\bar{C}})^2$
1	36	1288.5	1201.9	1245.2	4.9	4674.36	-0,2100	0,0441
2	36	719.7	722.1	720.9	0.2	927.51	0,2995	0,0897
3	33	1226.7	1233.0	1229.9	0.4	4609.42	-0,1951	0,0381
4	33	887.2	910.7	899.0	1.9	1196.93	0,1264	0,0160
5	30	1254.5	1251.0	1252.8	0.2	4923.25	-0,2173	0,0472
6	30	739.9	752.9	746.4	1.2	915.91	0,2747	0,0755
7	31	1229.0	1231.6	1230.3	0.1	4627.90	-0,1955	0,0382
8	31	824.5	818.8	821.7	0.5	1035.75	0,2016	0,0406
9	33	1265.6	1257.2	1261.4	0.5	4522.62	-0,2257	0,0509
10	33	717.2	707.5	712.4	1.0	1318.01	0,3078	0,0947
11	22	1285.5	1271.4	1278.5	0.8	4980.65	-0,2423	0,0587
12	22	522.2	519.3	520.8	0.4	858.17	0,4939	0,2439
13	—	3.2 ²⁾	—	3.2	—	6.31	0,9969	0,9938
14	19	1262.2	1250.2	1256.2	0.7	4448.33	-0,2206	0,0487
15	19	857.3	859.0	858.2	0.1	1332.36	0,1661	0,0276
16	15	1340.4	1344.6	1342.5	0.2	4234.25	-0,3045	0,0927
17	15	819.2	809.8	814.5	0.8	1701.16	0,2086	0,0435
18	41	5.3	5.4	5.4	1.5	9.22	0,9948	0,9896
19	39	1100.7	1102.6	1101.7	0.1	4234.60	-0,0705	0,0050
20	36	1230.6	1215.3	1223.0	0.9	4597.38	-0,1884	0,0355
21	36	693.3	701.2	697.3	0.8	1048.46	0,3224	0,1039
22	33	1242.8	1250.5	1246.7	0.4	4602.57	-0,2114	0,0447
23	33	503.9	512.7	508.3	1.2	827.36	0,5061	0,2561
24	31	—	1453.4	1453.4	—	6436.96	-0,4123	0,1700
25	31	74.0	71.4	72.7	2.5	42.73	0,9294	0,8638
26	29	1451.0	1456.3	1453.7	0.3	6159.76	-0,4126	0,1702
27	29	16.3	23.5	19.9	25.8	8.92	0,9807	0,9618
28	26	1112.7	1082.9	1097.8	1.9	4188.32	-0,0667	0,0044
29	26	2.6	2.5	2.6	1.9	4.64	0,9975	0,9950
30	—	2.9 ²⁾	—	2.9	—	3.58	0,9972	0,9944
Total					51.2 (27 δ_A)	78477.39	+5,6307	7,6383

1) The 1. and 2. concentration determination were performed on different samples.

2) As not measured by laboratory B, the value of laboratory A has been taken.

$$\bar{C} = \frac{\text{Total amount of Pu of the campaign}}{\text{Total amount of fuel solution}} = 1029.13 \text{ } \mu\text{g Pu/g. solution}$$

Table 4 Single Batch Analysis Method
Data used for the Error Calculation

	Laboratory A		Laboratory B	
	Uranium	Plutonium	Uranium	Plutonium
Number of batches n	30	30	30	30
Number of samples per batch m	1	1	2	2
Number of measurements per sample l	1	1	1	1
\bar{y}^2 1)	0.231	0.247	0.234	0.255
\bar{y}^2 1)	0.031	0.033	0.032	0.035
Coefficient of variation of single volume measurement δ_{Vr}	0.0025	0.0025	0.0025	0.0025
Coefficient of variation of volume measurement calibration δ_{Vs}	0.001	0.001	0.001	0.001
Coefficient of variation of sampling error δ_I	0.012	0.018	0.012	0.018
Coefficient of variation of single concentration measurement δ_{Cr}	0.002	0.006	0.002	0.006
Coefficient of variation of concentration measurement calibration δ_{Cs}	0.003	0.003	0.003	0.003

1) Calculated from formula (2.11) using the values given in table 2 and 3 a/b

Table 5 Calculation of Coefficient of Variation of Single Batch Analysis Method according to Formula 2.9

Laboratory	Element	$\frac{\sum^2}{n} \delta_{Vr}^2 + \frac{\sum^2}{n} \delta_{Vs}^2 + \frac{\delta_I^2}{n m} + \frac{\delta_{Cr}^2}{n m l} + \delta_{Cs}^2 = \delta^2 \bar{C}$	$\delta \bar{C}$
A	U	$(0.05 + 0.03 + 4.80 + 0.13 + 9.00) \times 10^{-6} = 14.01 \times 10^{-6}$	0.37 %
A	Pu	$(0.05 + 0.03 + 10.80 + 1.20 + 9.00) \times 10^{-6} = 21.08 \times 10^{-6}$	0.46 %
B	U	$(0.05 + 0.03 + 2.40 + 0.07 + 9.00) \times 10^{-6} = 11.55 \times 10^{-6}$	0.34 %
B	Pu	$(0.05 + 0.04 + 5.40 + 0.60 + 9.00) \times 10^{-6} = 15.09 \times 10^{-6}$	0.39 %

Table 6 Ratios of the Concentration Determinations by the
two Laboratories A and B

$$r_{ij}(C) = \frac{C_{ij} \text{ (Lab. B)}}{C_{i..} \text{ (Lab. A)}}$$

Batch ¹⁾	Uranium		Plutonium	
	$r_{i1}(C)$	$r_{i2}(C)$	$r_{i1}(C)$	$r_{i2}(C)$
1	1.031	0.957	1.004	0.937
2	0.979	0.985	1.004	1.007
3	0.975	0.968	1.028	1.034
4	0.959	0.967	0.980	1.006
5	0.980	0.973	1.050	1.047
6	0.932	0.933	0.959	0.976
7	1.086	1.026	0.995	0.997
8	1.027	1.012	0.969	0.962
9	1.019	1.022	1.025	1.018
10	1.007	1.007	1.006	0.993
11	1.024	1.006	0.955	0.944
12	1.011	1.012	0.932	0.926
14	0.993	0.978	1.008	0.999
15	1.017	1.021	1.019	1.021
16	0.990	0.994	0.994	0.997
17	0.993	0.980	0.981	0.970
19	1.004	1.000	1.008	1.010
20	1.014	1.003	1.032	1.019
21	0.984	0.996	0.996	1.007
22	1.014	1.016	1.034	1.041
23	0.996	0.999	1.020	1.038
24	1.017	—	1.036	—
26	1.004	1.014	1.034	1.038
28	1.022	1.002	1.047	1.019
Total	24.078	22.871	24.116	23.006
Mean value	$\bar{r}(C) = 0.9989$		$\bar{r}(C) = 1.0026$	

1) The data of the batches 13, 18, 25, 27, 29 and 30 were omitted as they were not obtained by isotopic dilution analyses of laboratory A or not measured by laboratory B.

Table 7 Comparison of the Mean Values $\bar{r}(C)$ of the Ratios
of the Concentration Determinations and the Ratio $r(\bar{C})$
of the Mean Concentration Values calculated from
Single Batch Analyses
(Laboratory B / Laboratory A)

	$\bar{r}(C)$	$r(\bar{C})$	$\bar{r}(C) - 1$	$r(\bar{C}) - 1$
Uranium	0.9989	1.0035	-0.11 %	+0.35 %
Plutonium	1.0026	1.0102	+0.26 %	+1.02 %

Note: For the calculation of these values the data of the batches 13, 18, 25, 27, 29 and 30 were omitted as they were not obtained by isotopic dilution analyses of laboratory A or not measured by laboratory B.

Table 8a

Composite Sample Analyses for Uranium

Labo- ratory	Compo- site sample	Concentration $C_{I,II}$ [$\bar{m}g$ U/g solution]	Mean value C of concentration per laboratory [$\bar{m}g$ U/g solution]	Mean concentration ³⁾ calculated from single batch analyses for comparison [$\bar{m}g$ U/g solution]
B	I	168.19	168.20 ($\pm 0.40\%$) ¹⁾	164.15
B	II	168.21		
C	I	166.50	165.40 ($\pm 0.56\%$) ¹⁾	
C	I ²⁾	164.50		
C	II	165.20		

Table 8b

Composite Sample Analyses for Plutonium

Labo- ratory	Compo- site sample	Concentration $C_{I,II}$ [$\bar{\mu}g$ Pu/g solution]	Mean value C of concentration per laboratory [$\bar{\mu}g$ Pu/g solution]	Mean concentration ³⁾ calculated from single batch analyses for comparison [$\bar{\mu}g$ Pu/g solution]
B	I	1048.08	1046.75 ($\pm 0.61\%$) ¹⁾	1023.6
B	II	1045.42		
C	I	1061.00	1065.00 ($\pm 0.84\%$) ¹⁾	
C	II	1069.00		

1) Coefficient of variation as given by table 10

2) Repeated measurement of sample I

3) Mean value of concentrations determined by laboratory A and B according to the single batch analysis method.

Table 9 Composite Sample Technique
Data used for the Error Calculation

	Laboratory B		Laboratory C	
	Uranium	Plutonium	Uranium	Plutonium
Number of batches n	30	30	30	30
Number of samples per batch m	1	1	1	1
Number of aliquotations per sample p	2	2	2	2
Number of measurements per composite sample l	1	1	1 1)	1
\bar{y}^2 2)	0.233	0.251	0.233	0.251
\bar{y}^2 2)	0.032	0.034	0.032	0.034
Coefficient of variation of single volume measurement δ_{Vr}	0.0025	0.0025	0.0025	0.0025
Coefficient of variation of volume measurement calibration δ_{Vs}	0.001	0.001	0.001	0.001
Coefficient of variation of single aliquotation δ_{wr}	0.0025	0.0025	0.0025	0.0025
Coefficient of variation of aliquotation calibration δ_{vs}	0.0015	0.0015	0.0015	0.0015
Coefficient of variation of sampling error δ_I	0.012	0.018	0.012	0.018
Coefficient of variation of single concentration measurement δ_{Cr}	0.002	0.006	0.006	0.010
Coefficient of variation of concentration measurement calibration δ_{Cs}	0.003	0.003	0.003	0.003

- 1) For this error calculation, the duplicate analysis of the composite sample I has not been taken into consideration .
- 2) The mean values from the laboratories A and B of the single batch method (table 4) have been used.

Table 10 Calculation of Coefficient of Variation of Composite Sample Analyses according to Formula 2.10

Laboratory	Element	$\frac{\bar{y}^2}{n} (\delta_{Vr}^2 + \frac{\delta_{Vf}^2}{p}) + \bar{y}^2 (\delta_{Vs}^2 + \delta_{vs}^2) + \frac{\delta_I^2}{n \cdot m} + \frac{\delta_{Cr}^2}{m \cdot p \cdot l} + \delta_{Cs}^2$	$= \delta^2 C$	δC
B	U	(0.07 + 0.10 + 4.80 + 2.00 + 9.00) x 10 ⁻⁶	= 15.97 x 10 ⁻⁶	0.40 %
B	Pu	(0.08 + 0.11 + 10.80 + 18.00 + 9.00) x 10 ⁻⁶	= 37.99 x 10 ⁻⁶	0.61 %
C	U	(0.07 + 0.10 + 4.80 + 18.00 + 9.00) x 10 ⁻⁶	= 31.97 x 10 ⁻⁶	0.56 %
C	Pu	(0.08 + 0.11 + 10.80 + 50.00 + 9.00) x 10 ⁻⁶	= 69.99 x 10 ⁻⁶	0.84 %

Table 11 Comparison of Analytical Efforts

Method	Number of Samples taken per batch	Total number of samples	Number of composite samples prepared	Number of analyses for concentration determination	Accuracy calculated according to formulas (2.9) and (2.10) for Pu-concentration	Data taken from the measurements of
Single batch method	1	30	-	30	0.46 %	laboratory A
Composite sample technique "I"	1	30	1	10	0.48 %	laboratory B
Composite sample technique "II"	4	120	4	4	0.46 %	laboratory B

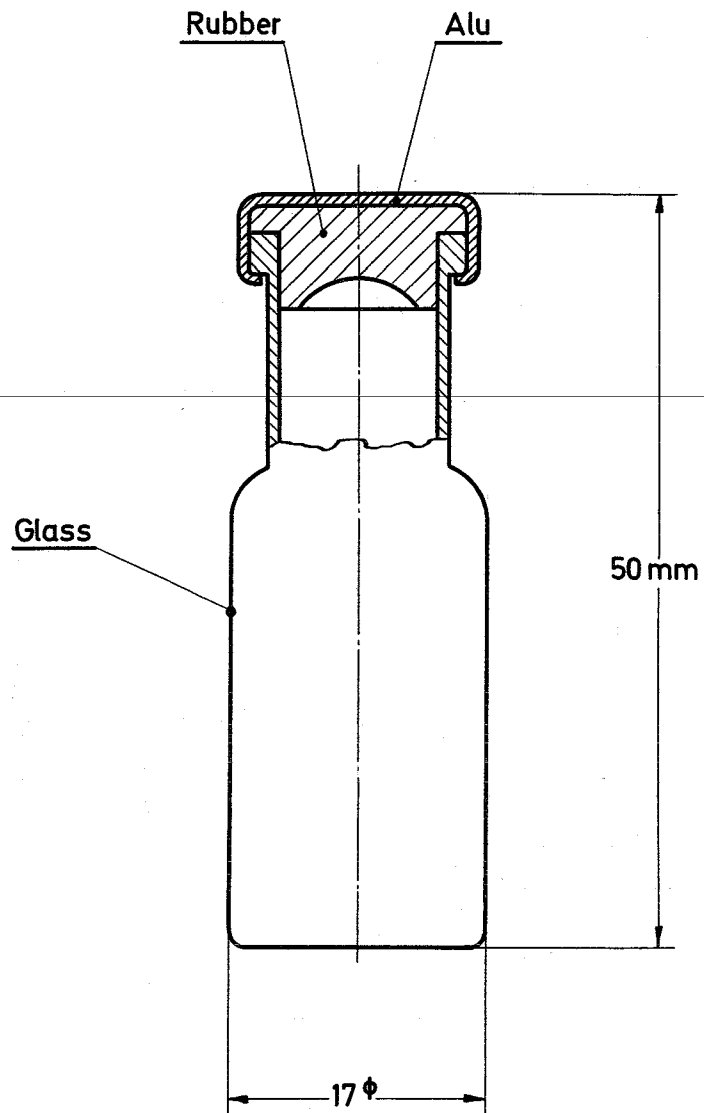


Fig.1 Sample bottle

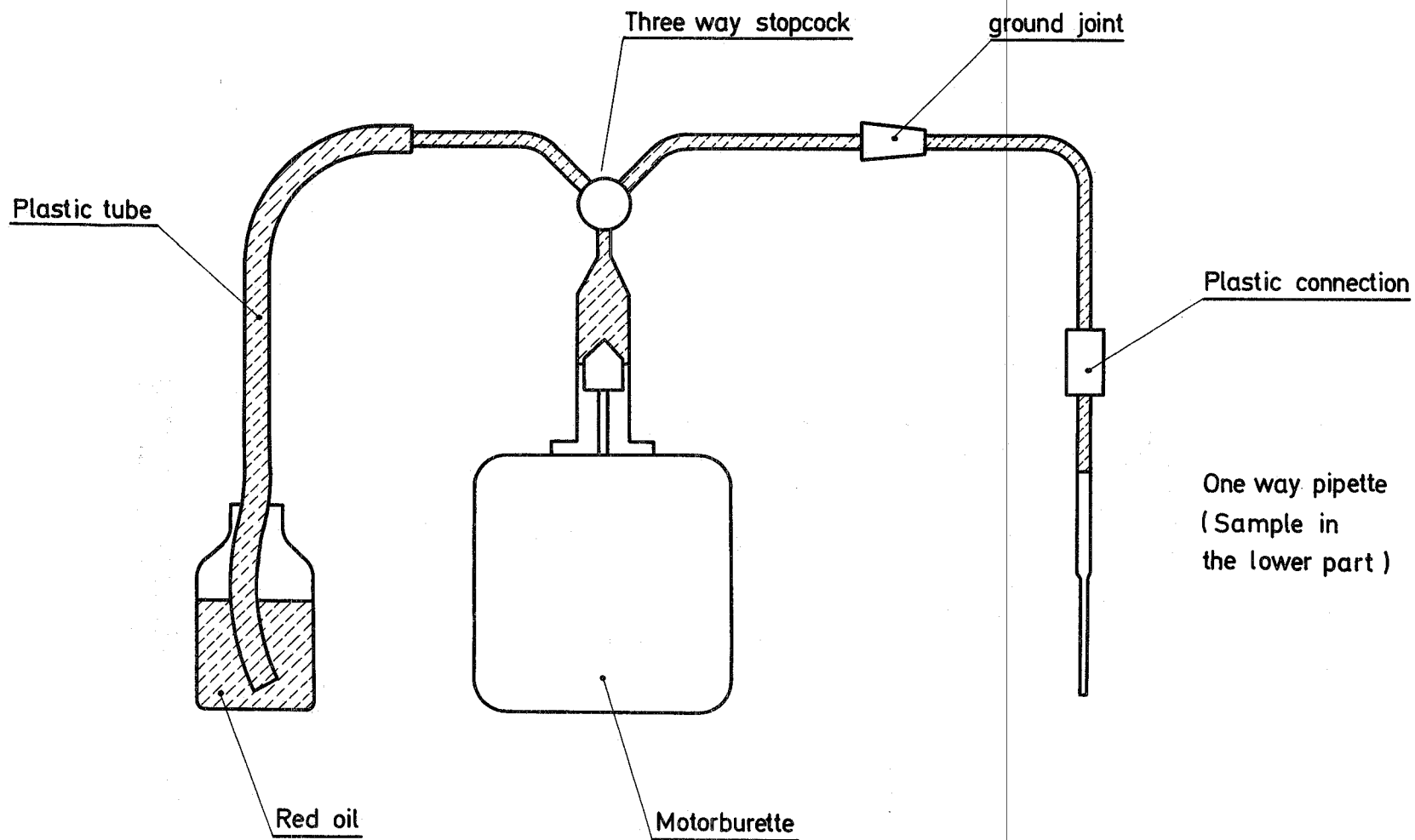


Fig. 2 Aliquotation Device

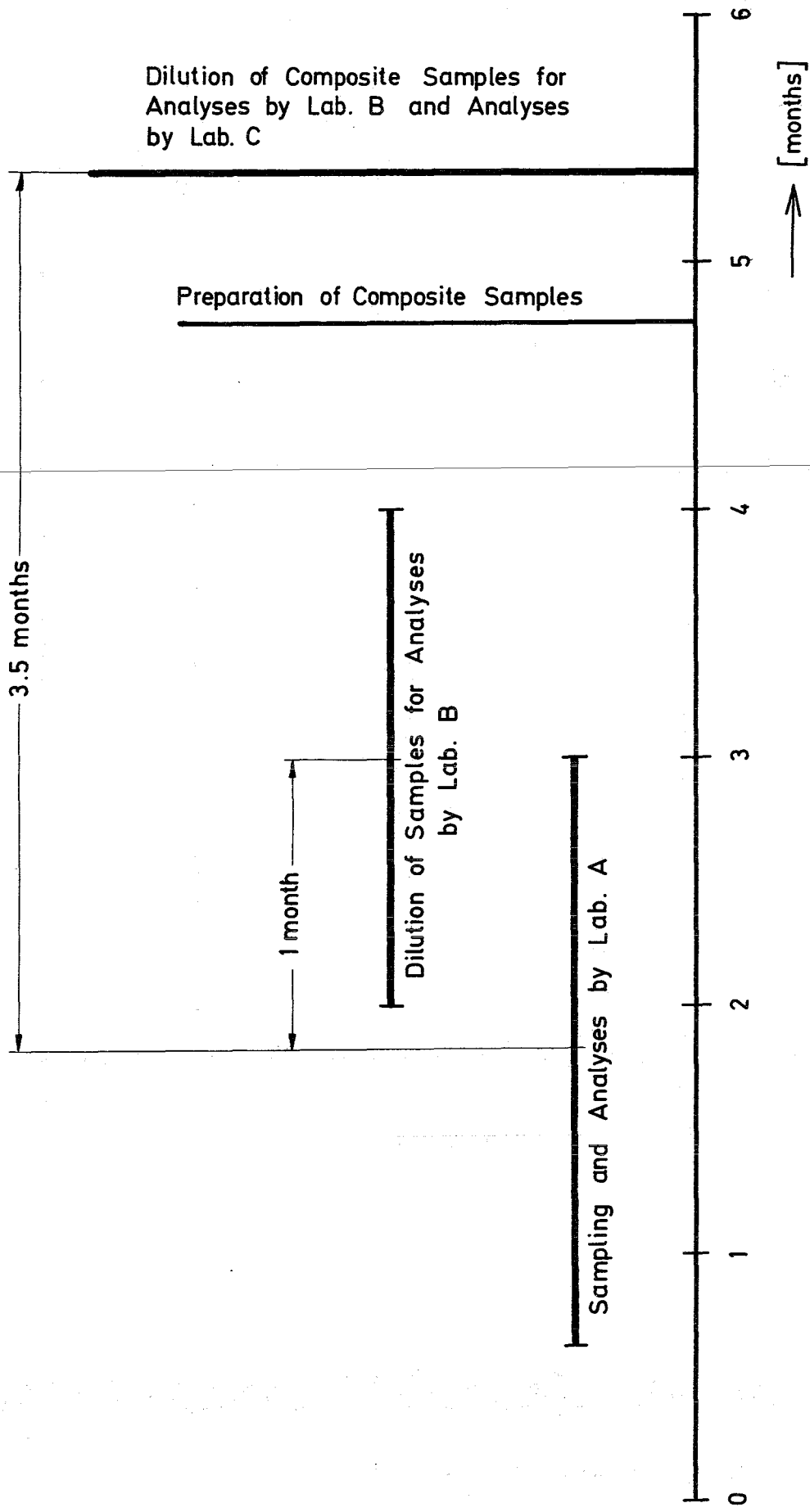


Fig.3 Time Schedule of Sampling and Analyses

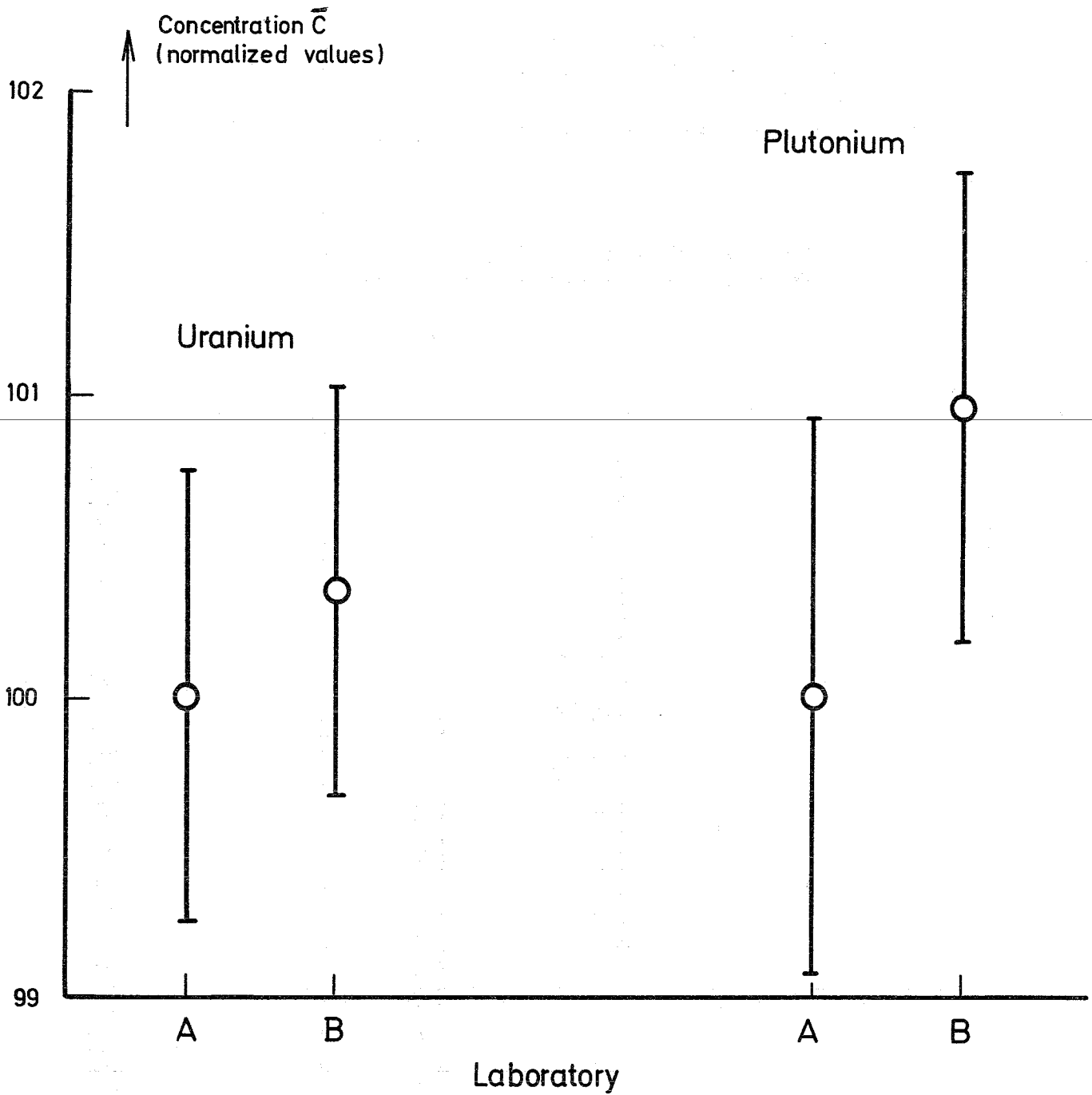


Fig.4 Results of Single Batch Analyses Method

(Indicated error ranges : $\pm 2\sigma$)

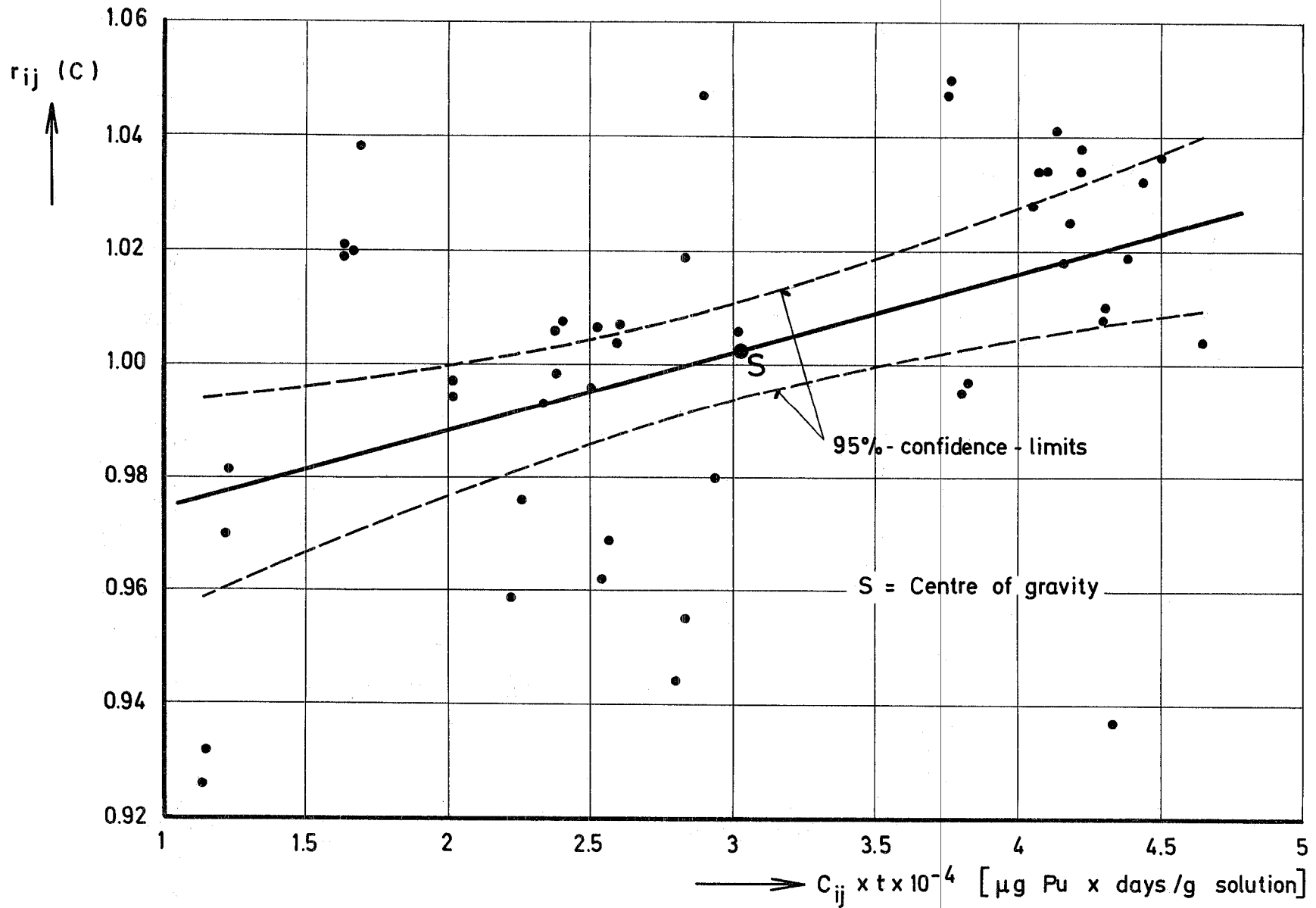


Fig. 5 Regression of the Concentration Ratios $r_{ij} (C)$ versus the Product of the Concentration C_{ij} . (Lab. B) and Sample Age t .

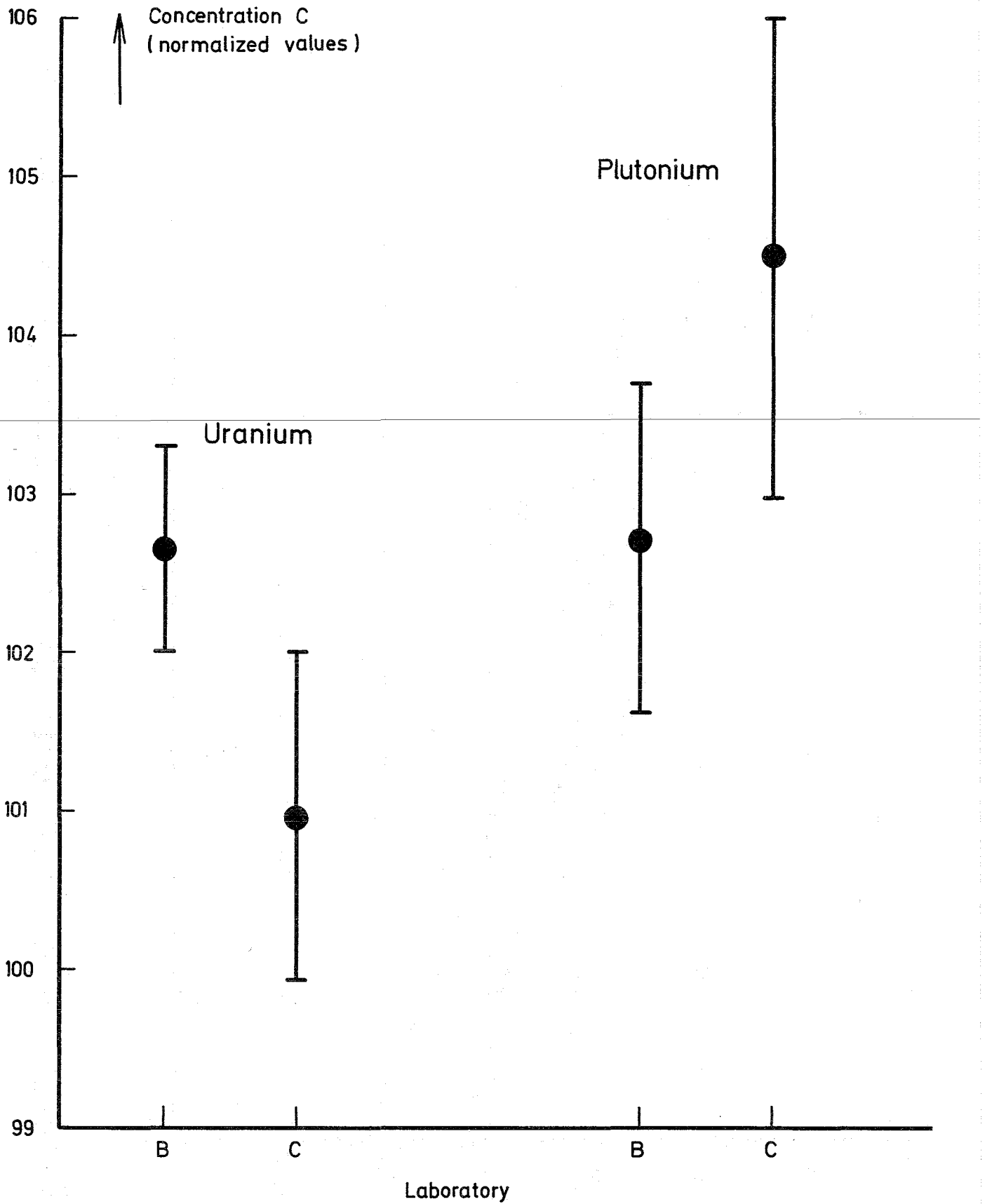


Fig.6 Results of Composite Sample Analyses
(Indicated error ranges : $\pm 2\sigma$)

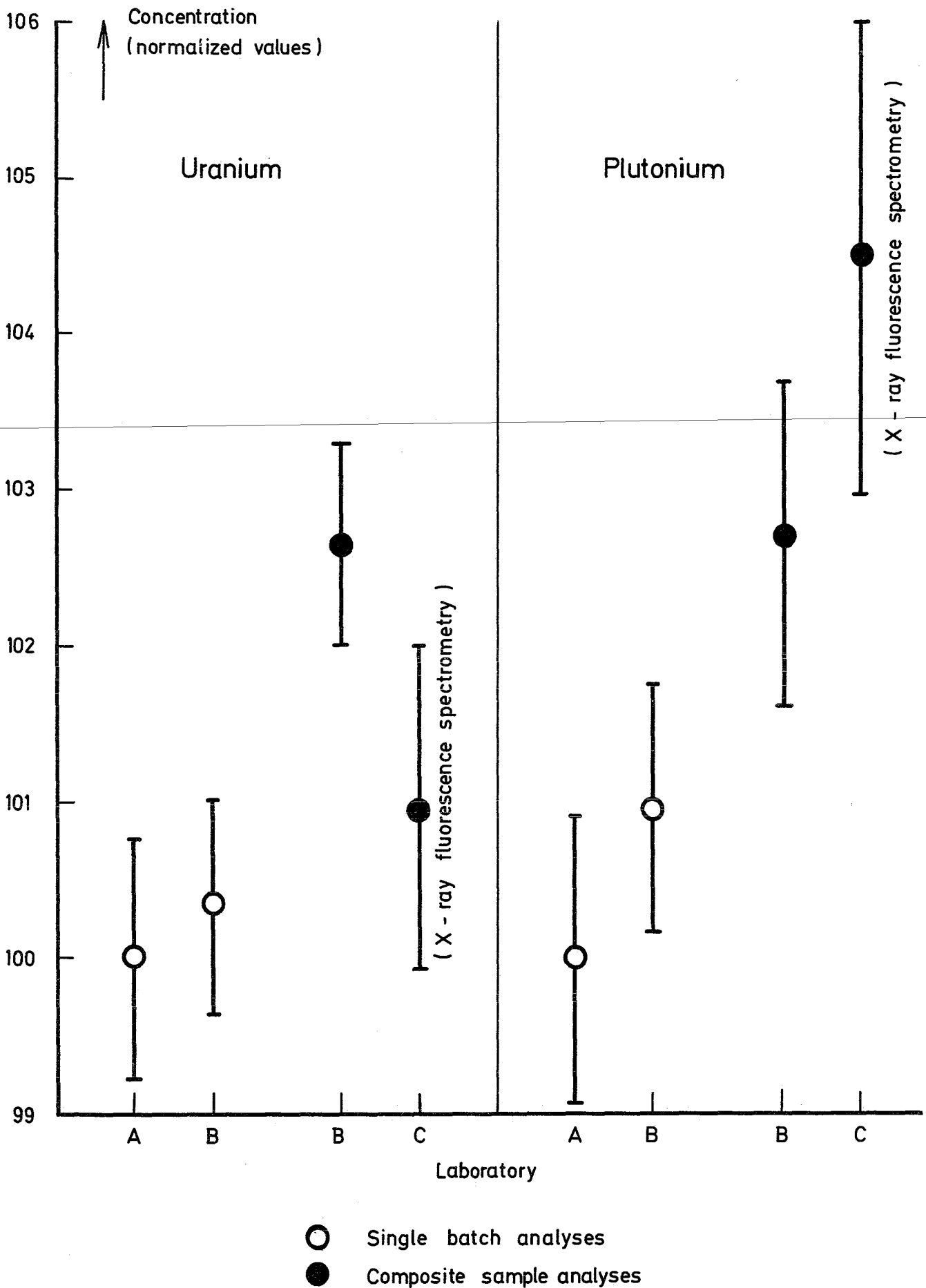


Fig.7 Results of Single Batch and Composite Sample Analyses

(Indicated error ranges : $\pm 2\sigma$)

