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SAVANNAH RIVER LABORATORY

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MEMORANDUM

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THE USE OF PULSED LASER FLUORIMETRY FOR URANIUM ANALYSIS

Summary

Pulsed laser fluorimetry was shown to be a sensitive, rapid method for determining low levels of uranium in aqueous solutions. Uranium concentrations in the 0.5 - 20 ppb range were analyzed with a Scintrex UA-3 uranium analyzer, which employs a nitrogen laser excitation source. Interference tests were performed to assess the effects of various chemical species on uranium analysis. Of the species typically found in uranium samples at SRL, only high acid concentrations posed a problem which could not be overcome by a standard additions method, but modifications to sample preparation methods should alleviate this problem. Because the Scintrex instrument is not affected by the same types of interferences which plague the fused pellet technique now employed for uranium determinations, its use would extend analysis capabilities now available for some sample matrices. Suggestions are given for the fabrication of a pulsed laser uranium analysis system in which all components, except the sample cell, are external to the containment. The use of the UA-3 in containment would pose problems when repair and replacement was necessary, because the whole unit would be in containment.

Introduction

New methods for uranium determination are being sought to improve both precision and sensitivity of the techniques now employed at SRL-SRP. Approximately 50 samples are submitted to ACD for uranium analysis each month. The current method employed for these determinations is the fused pellet technique in which the uranium is first extracted from the sample then deposited on NaF pellets for fluorimetric analysis. The need for precise control of all operations involved in preparation and sintering of these pellets gives this technique poor reliability. In addition, the fused pellet technique is hindered by many chemical interferences.

The Scintrex UA-3 uranium analyzer utilizes pulsed laser fluorimetry to determine trace levels of uranium. The instrument was originally produced to provide in-field uranium analyses of natural water (1,2) and is currently used in the NURE program at SRL. Recently, this instrument was evaluated at NBL for the determination of uranium in safeguards samples and was found to be superior to the fused pellet technique (3). The heart of the UA-3 is a low-power, pulsed nitrogen laser which acts as the excitation source for the unit. The 337.1 nm output of the laser excites fluorescence from a uranyl complex which is formed when a sodium pyrophosphate reagent (FLURAN) is added to the sample solution. A gated detection system measures the intensity of the fluoresence, which is proportional to the uranium concentration.

In this study, a UA-3 unit borrowed from the NURE group was evaluated with respect to the type of samples submitted for uranium analysis at SRL. Since subsequent use required a non-contaminated instrument, samples containing plutonium were not examined. Other cations and anions known to be present in typical samples were studied to assess their effects on uranium analysis with the UA-3.

Results

The procedure followed for the anaylsis was similar to that suggested in the UA-3 manual. First, a 5 ml aliquot of a standard or sample was pipetted into the cell. After inserting the cell, any background fluorescence was nulled using the blank control. Next, 750 µl of FLURAN were added and the sample mixed. The signal produced after FLURAN addition was recorded or used to calibrate the instrument. If the standard addition technique was utilized, a 25 µl aliquot of 100 ppb U was added and another reading recorded.

Highly linear calibration curves were obtained from the Scintrex unit in the 0.5 - 20 ppb U (Figure 1). Data analysis using a linear least squares algorithm gave correlation coefficients greater than 0.995 for both plots. Unfortunately, the zero setting and calibration for the two scales were different. Scale changes during the analysis would result in error unless a separate calibration was used for each scale. The meter readings on the 0 - 20 ppb U scale fluctuated more than the low concentration scale, making analyses easier at low concentrations. High scale readings were used to estimate the dilution factors required to place the sample reading on the low scale.

When a standard addition technique was utilized, the recovery of the standards ranged from 86% to 111%, with a mean of 101%. Several sets of samples containing 1.0 ppb U were analyzed, giving a typical relative standard deviation of ±10%. This is comparable to the fused pellet technique, which gives a ±10% RSD in the analysis of 20 ppb U (4).

Interference studies were performed to determine the effect of chemical species found in typical SRL uranium samples on the response of the Scintrex instrument. Uranium solutions (1.0 ppb) containing a selected cation or anion were made to give relative concentration ratios up to 40,000:1. These solutions were then analyzed using standard additions to give the results shown in Table 1. None of the selected ions produced an interference at a concentration ratio of 1,000:1. At a 10,000:1 ratio, both sulfate and ammonium produced enhanced signals. The cause for this enhancement was not determined, but modifications to the standard addition technique should allow correction for the enhancement. When a 40,000:1 concentration ratio was present, solutions containing Fe^{+3} and NO_2^- quenched the uranium fluorescence. For both these cases, application of the standard addition technique enabled the determination of the solution's uranium content.

The most severe quenching effect encountered with the UA-3, was that produced by the presence of acid. At acid concentrations greater than 0.1 M, accurate analyses could not be performed. At lower concentrations, the fluorescence signal was depressed, but standard addition techniques allowed the determination of the uranium content. At higher concentrations of acid (up to 2.0 M), the quenching of the fluorescence produced such low meter readings, that the meter could not be read very accurately, producing errors in the analysis. These problems could be overcome by using a more sensitive readout device, or adjusting the pH of the sample prior to analysis.

Discussion

Procedural Considerations

The results obtained from the Scintrex UA-3 have shown that pulsed laser fluorimetry is a viable alternative to the fused pellet technique for uranium analysis in aqueous solutions. Using the procedure outlined above, the relative standard deviation of the method (±10%) matches that of the fused pellet technique. A procedure developed at NBL has increased the precision to ±5%, by weighing the amount of the sample or standard addition spike added to the cell and by more efficient mixing of the FLURAN buffer with the sample (3).

The concentration detection limit of the UA-3 is lower than that of the fused pellet technique (0.10 ppb vs. 1.0 ppb U). However, when absolute quantities of uranium are considered, the fused pellet technique is more sensitive and can detect 0.05 ng of uranium compared to 0.3 ng for the Scintrex instrument. The relatively poor performance of the UA-3 in this respect is linked to the small interaction volume of the laser beam in the sample. Only a fraction of the 5 ml sample is encountered by the laser radiation and analyzed when the 20 mm x 10 mm rectangular cells supplied with the unit are utilized. The use of smaller sample volumes and cells which maximize the fraction of the sample that is actually analyzed should improve the absolute detection limit of the instrument. For the laser-based method, analysis time should be less than 10 minutes per sample after dilutions, if triplicate determinations are performed. The pellet method, on the other hand, requires additional time for extractions and proper preparation of the pellets.

Changes in the sample preparation procedure and labware should increase reproducibility. Use of only polyethylene labware should decrease any errors produced by loss of uranium through absorption on glass surfaces. In this study, solutions were made up in glass volumetric ware and stored in polyethylene bottles. The procedure could also be modified to eliminate some predetermination dilutions by adding a sample aliquot directly to the cell, followed by a preset volume of water to accomplish dilution. The effect of these changes on the precision of the method will need to be assessed by further development work.

Chemical Effects

The pulsed laser fluorimetry technique is not plagued by the same types of interferences as the fused pellet method. As shown in Table 1, the presence of some species, such as thorium, which produce severe interferences in the pellet method, have no effect on the UA-3 analysis. The NBL study also included a chemical interference test and found no interference from Al, Ca, Ce, Cr, Cu, Mn, Ni, Si, Ti, V, Zn, Zr at a concentration ratio of 200:1 relative to the uranium content. In the same study, the fused pellet technique exhibited interferences from Ce, V, and Th (200:1 concentration ratio) which could not be overcome by standard addition methods (3).

The effect of acid concentration and the problem of organic fluorescence are two major drawbacks to the laser fluorimetry method. High acid concentrations quench the uranium fluorescence. A pH adjustment should eliminate this interference, and should be as easy to perform as the extraction required for the fused pellet procedure. Adjustment of the pH of the sample might be easily accomplished by adding a non-fluorescent indicator to the dilution flask and adding base until a proper color change occurred. If a suitable indicator cannot be found, a pH meter would be required. For aqueous solutions, no additional sample preparation is required after proper dilutions are obtained. Solutions with high organic content will create an interference due to the fluorescence of the organic compounds. Due to the limited availability of the Scintrex unit, the effect of organic was not studied. More development time is needed to properly assess the extent of these problems, and devise methods for their solution.

Instrumental Considerations

If the Scintrex UA-3 instrument is employed for routine analysis, certain modifications should be made to improve the precision of the method. As suggested in the NBL report (3), the front panel meter, which indicates the fluorescence intensity, should be replaced by a more easily read device such as a digital meter. This new readout device should have sufficient range to enable low level readings, such as those encountered when an interference is present, to be easily obtained. The sample insertion mechanism should also be revised to include a shutter for the detector. At present, the detector must be turned off whenever the sample compartment is opened. The photomultiplier is never allowed to stabilize, leading to additional noise in the signal.

The fabrication of a pulsed laser fluorimetry system would provide a uranium analyzer tailored to the needs at SRL-SRP. This preliminary study has shown that the pulsed laser fluorimetry method can be applied to many of the uranium determinations currently processed using the fused pellet technique. A system utilizing the pulsed laser technique could be fabricated with all or most of the electronics external to a containment structure. Figure 2 shows two possible configurations for a laser system. Figure 2a requires only one window in the side of the containment. All components except the cell and detector assembly are external to the containment. A system in which the detector is all external is shown in Figure 2b. An increase in sensitivity should be possible if a higher power laser is used, but some power will be lost through reflection from the additional optical components in the system. The electronic portion of the system would incorporate the suggested modifications to the Scintrex unit to enable higher precision analyses.

The cost of assembling a custom instrument is comparable to the price of a Scintrex UA-3 instrument ($16,000). In addition, the capabilities of the custom system could be expanded to include analyses of other materials with the addition of a dye laser (an additional $6000). The present fused pellet system has two components, the fluorometer and the pellet fusion oven. The highly mechanized oven ($7000) has been designed and fabricated at SRL. The fluorometer can be purchased or fabricated in-house for a similar amount, making the total cost of a new custom-built instrument ($14,000) comparable to the laser-based systems.

Equipment necessary to investigate the type of results obtainable from the custom-built laser system will soon be available at SRL. The equipment is part of the instrumentation being assembled for laser-excited atomic fluorescence spectrometry. Once the installation is complete, only a few modifications will be required to utilize the system to determine uranium. Studies are planned to further investigate the sensitivity and precision of uranium analyses obtainable with a laser-based system and to evaluate the possible optical systems required to use the instrument with samples in containment.

Conclusions

Pulsed laser fluorimetry is a sensitive method for the determination of uranium in aqueous samples. Although high acid and organic content hinder this method, other factors which interfere with the fused pellet technique (such as high thorium content) have no effect on the analysis.

A commercial pulsed laser instrument, the Scintrex UA-3 analyzer, was evaluated and found to possess sensitivity and precision similar to those of the fused pellet technique. The Scintrex unit could be utilized in routine analysis, with a few minor modifications, but the cost and difficulty of repair and laser replacement make its use less attractive. The fabrication of a pulsed laser system with all components, except the sample cell, external to any containment would provide uranium analyses with precision comparable or better than that available with the fused pellet method, while permitting easy access for service. Cost exclusive of containment is estimated to be $16K.

KAS:lhl

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3. Collins, L. H. and A. C. Zook, "Applications of a Direct Method for the Determination of Trace Uranium in Safeguards Samples by Pulsed Laser Fluorimetry", Proceedings of the American Nuclear Society Topical Conference on Measurement Technology for Safeguards and Material Control, Kiawah, SC, November, 1979.
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TABLE 1

EFFECT OF CHEMICAL SPECIES ON THE ANALYSIS OF URANIUM VIA THE SCINTREX UA-3 ANALYZER

	Concentration Ratios		
Species	1,000:1	10,000:1	40,000:1
Cl^-	N	N	N
DBP-MBP	N	N	N
Fe^{+3}	N	N	Q
Na^+	N	N	N
NH_4^+	N	E	E
NO_2^-	N	N	Q
NO_3^-	N	N	N
PO_4^{3-}	N	N	N
SO_4^{2-}	N	E	E
Th^{+4}	N	N	N

N = No effect

E = Enhanced signal

Q = Quenched signal

Figure 1

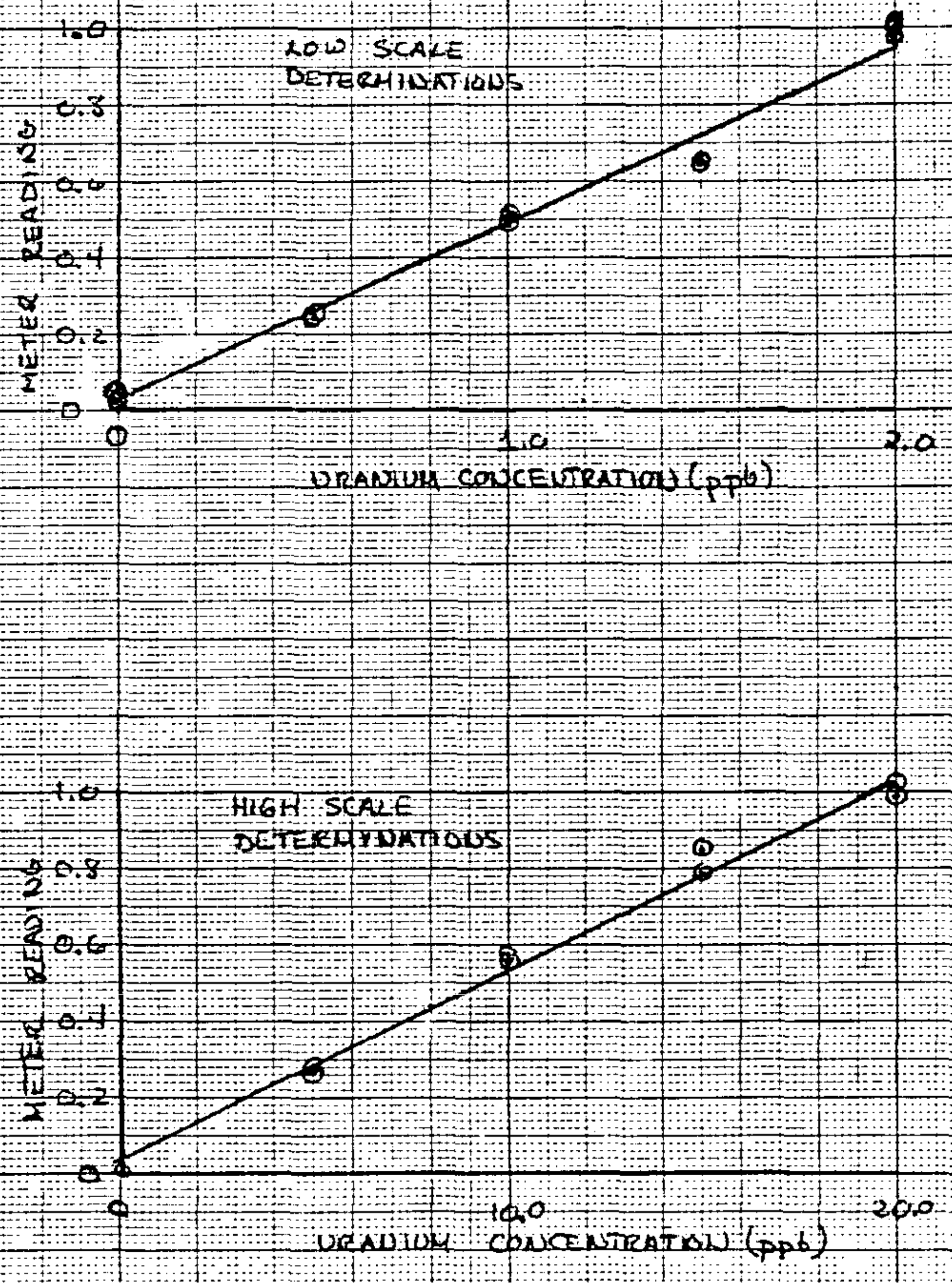
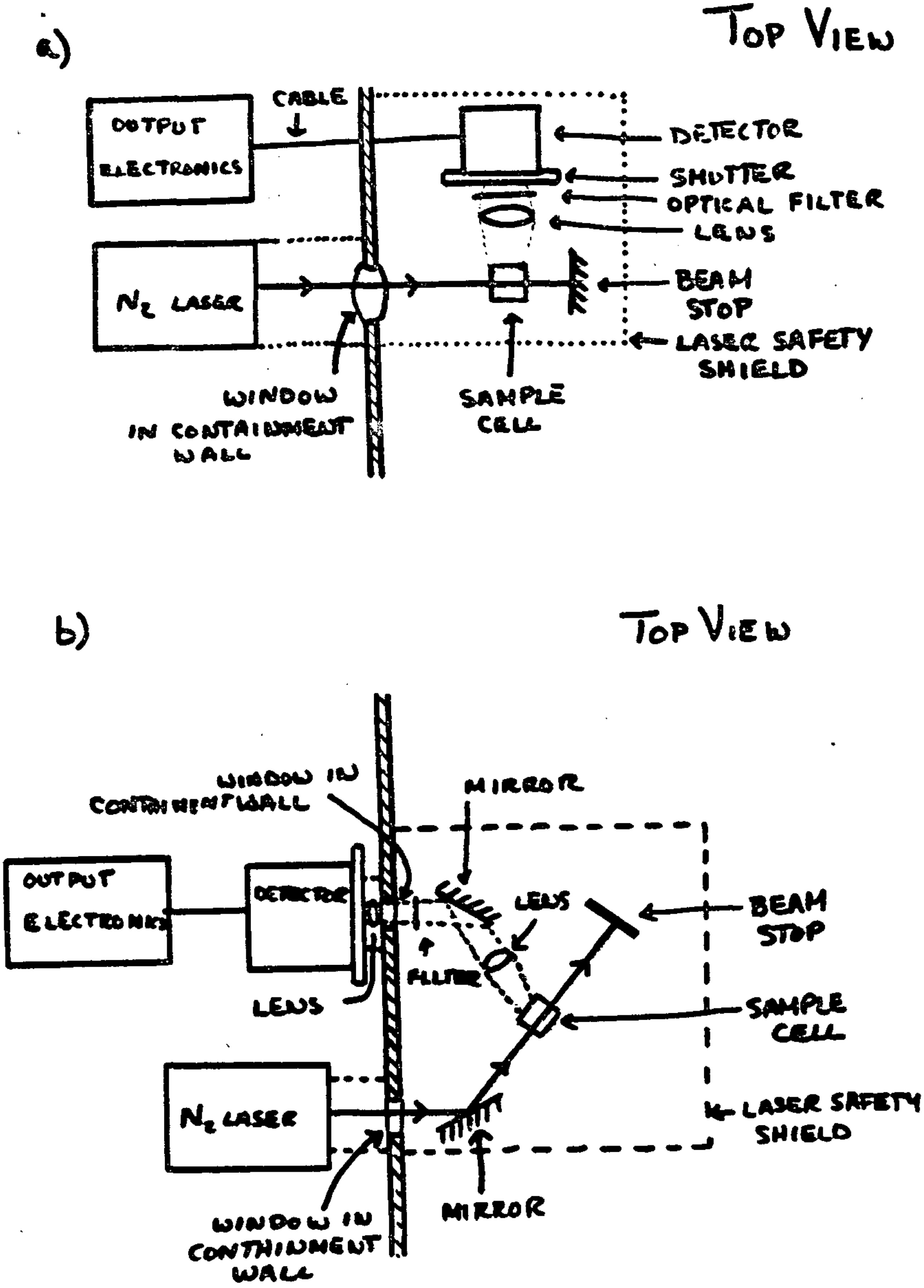

LOW SCALE DETERMINATIONS
METER READING
1.0
0.8
0.6
0.4
0.2
0
0
1.0
2.0
URANIUM CONCENTRATION (ppb)
HIGH SCALE DETERMINATIONS
METER READING
1.0
0.8
0.6
0.4
0.2
0
0
10.0
20.0
URANIUM CONCENTRATION (ppb)

FIGURE 2


a)
TOP VIEW
CABLE
OUTPUT ELECTRONICS
DETECTOR
SHUTTER
OPTICAL FILTER
LENS
N_2 LASER
BEAM STOP
LASER SAFETY SHIELD
WINDOW IN CONTAINMENT WALL
SAMPLE CELL
b)
TOP VIEW
WINDOW IN CONTAINMENT WALL
MIRROR
OUTPUT ELECTRONICS
DETECTOR
LENS
BEAM STOP
FILTER
LENS
SAMPLE CELL
N_2 LASER
LASER SAFETY SHIELD
WINDOW IN CONTAINMENT WALL
MIRROR