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European Microbeam Analysis Society

EMAS 2025

18th

EUROPEAN WORKSHOP

on

MODERN DEVELOPMENTS AND APPLICATIONS IN MICROBEAM ANALYSIS

11 to 15 May 2025
at the
TecnoCampus
Mataró (Barcelona), Spain

Organized in collaboration with the
Universitat de Barcelona, Spain

EMAS
European Microbeam Analysis Society eV
www.microbeamanalysis.eu/

This volume is published by:
European Microbeam Analysis Society eV (EMAS)
EMAS Secretariat
c/o Eidgenössische Technische Hochschule, Institut für Geochemie und Petrologie
Clausiusstrasse 25
8092 Zürich
Switzerland

ISBN 978 90 8227 6985
NUR code: 972 – Materials Science

DEVELOPMENT OF CORRELATED FIB-TOF-SIMS AND SEM-AM METHODS FOR THE SEARCH FOR, AND CHARACTERISATION OF, ENRICHED URANIUM PARTICLES

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1. ABSTRACT

As part of a global initiative to detect and monitor uranium use in nuclear facilities, the International Atomic Energy Agency (IAEA) collects environmental samples from various countries and analyses them for the presence of man-modified uranium and other nuclear fuel cycle materials. For example, highly enriched uranium can be associated with undeclared nuclear material or activities, making its detection critical for nuclear non-proliferation efforts. The paper presents an advanced analytical workflow that combines automated mineralogy, FIB-ToF-SIMS (focussed ion beam-time of flight secondary ion mass spectrometry), and LG-SIMS (large geometry secondary ion mass spectrometry) to efficiently identify and characterise uranium-containing particles in field samples. This integrated workflow automates time-consuming aspects of particle analysis, significantly improving the speed and precision of detecting uranium. I t also provides detailed, complementary data on particle morphology and the chemical elements associated with each particle. The approach was shown to effectively identify and characterise particles containing enriched uranium, offering an in-depth understanding of the material's composition. The workflow's efficiency and precision make it a potentially valuable tool for nuclear material monitoring and non-proliferation efforts.

2. INTRODUCTION

The International Atomic Energy Agency (IAEA) conducts various types of environmental sampling as part of its nuclear safety, security, and safeguards efforts. These activities help ensure compliance with international non-proliferation treaties and prevent the unauthorized use of nuclear materials.

As part of its safeguards system, the IAEA collects environmental samples from nuclear facilities to detect uranium and plutonium isotopes, as well as other radioactive materials. This aids in identifying the use of enriched uranium and other materials related to nuclear activities. Routine environmental sampling is conducted to verify adherence to the Treaty on the Non-Proliferation of Nuclear Weapons (NPT) and other agreements, particularly in regions where compliance is uncertain or disputed.

One of the key techniques for particle analysis in environmental samples is large geometry secondary ion mass spectrometry (LG-SIMS), which scans thousands of particles for uranium before performing precise isotopic composition analysis. While effective, this method lacks complementary information about particle morphology and associated elements, making data correlation challenging.

Scanning electron microscopy (SEM) with energy-dispersive X-ray spectrometry (EDS) offers non-destructive, high-resolution particle analysis, providing morphology and major element composition. Backscattered electron (BSE) detection enhances contrast based on atomic

number, allowing uranium-containing particles to appear brighter. Despite its utility, SEM analysis is time-consuming due to the need to scan many particles and correlate their locations across microscopy and mass spectrometry methods.

SEM-based automated mineralogy (SEM-AM) enables rapid, operator-free analysis of solids and powders [1, 2]. By combining BSE imaging and EDS spectra, SEM-AM classifies minerals in a sample. Instruments equipped with four EDS detectors and high electron beam currents achieve detection rates exceeding 500,000 counts per second, allowing large-area scans with minimal intervention [1]. Using a calibrated BSE signal threshold to target only bright phases for X-ray analysis significantly reduces data collection time. SEM-AM has been successfully applied to uranium ores [3] and filter particles [4], demonstrating its potential for IAEA environmental monitoring.

While SEM-AM detects uranium-bearing particles, it does not characterise them in the context of nuclear material. The $^{235}U/^{238}U$ isotope ratio provides insights into a particle's provenance and synthesis method. Natural uranium contains 0.72 % ^{235}U [5], while low-enriched uranium (used in reactors) has 2 - 20 % ^{235}U, and highly enriched uranium (used in weapons) contains 20 - 85 % ^{235}U.

Mass spectrometry techniques such as LG-SIMS and time-of-flight secondary ion mass spectrometry (ToF-SIMS) enable isotope ratio measurements of individual particles. ToF-SIMS detectors integrated with dual-beam focussed ion beam (FIB)-SEM instruments allow simultaneous electron microscopy and mass spectrometry [6, 7]. This FIB-ToF-SIMS method achieves ≤ 50 nm lateral resolution with a mass resolution of 800 [7]. Combining SEM-EDS and FIB-ToF-SIMS enables high-resolution imaging, semi-quantitative chemical analysis, and isotope ratio measurement. However, due to modest mass resolution and limited sensitivity, ToF-SIMS is insufficient for precise isotopic quantification, making LG-SIMS the preferred method for accurate uranium isotope determination. Automated LG-SIMS screening routines [8] facilitate rapid detection of uranium-bearing particles, though high-resolution imaging and elemental analysis must be conducted separately.

This paper presents a workflow for analysing environmental monitoring samples from nuclear facilities using SEM-AM, FIB-ToF-SIMS, and LG-SIMS. Results from SEM-AM and FIB-ToF-SIMS are detailed, with subsequent LG-SIMS analyses forming part of the discussion.

3. METHODS

3.1. Sample preparation

The samples consist of cotton swipes that contain varying amounts of particles, which may include uranium and other substances relevant to nuclear safeguards. The identity of the sample

and its origin are not divulged to the analytical laboratories. The sample was mounted on a 25 mm diameter silicon wafer substrate which is suitable for use in the SIMS instrument. The preparation protocol involves the transfer of particles from the cotton swipe to the planchet for analysis. This technique uses the vacuum impactor method where particles are sucked off the swipe and deposited onto a sticky polymer on the planchet surface. The polymer is then baked off, leaving the particles on the planchet.

3.2. Automated mineralogy

Automated mineralogy was performed using a TESCAN TIMA3 SEM-AM at the John de Laeter Centre, Curtin University. The entire silicon wafer was analysed by stage mapping with a field of view of 600 µm and a pixel size of 0.5 µm (total of 905 fields mapped). An electron beam energy of 15 keV and a current of 3.3 nA was used. X-rays were detected with four PulseTor 30 EDS detectors. BSE and elemental X-ray maps were calculated from the output and used with parameterised X-ray intensity brackets from a mineral database to define phases in each pixel. The fields are then stitched together to form a sample scale mosaic. A bright phase analysis routine was used for the search of uranium particles with the BSE threshold set to 75 (relative to reference Pt metal signal).

3.3. FIB-ToF-SIMS

A Tescan Lyra3 FIB-SEM fitted with a Tofwerks compact-time of flight detector was used for FIB-ToF-SIMS analysis. A Ga^+ primary beam with an energy of 30 kV and current of 75 pA was used to raster a 10 × 10 µm area. Positive ions up to a mass of 340 mass/charge were collected. Data was processed with Tofwerks ToF-SIMS Explorer version 1.4.

4. RESULTS

A correlated microanalysis workflow involving search, targeted characterisation and isotopic measurement of uranium particles is required for the comprehensive analysis of environmental samples. The initial detection of uranium-bearing particles is achieved with SEM-AM, a fast, non-destructive method for automated phase identification. A bright phase search method, which targets high atomic number particles based on backscattered electron (BSE) signal, can scan up to 12 planchets (or more with specialised sample holders) without operator intervention. Additionally, complementary information, including mineralogy of other grains and particle size, can be derived from the data. The stage positions of identified uranium particles are recorded in a spreadsheet and can be transferred to other instruments. A SEM-AM facility can analyse over 50 planchets per week, representing significant throughput for environmental monitoring studies.

Particles identified as uranium-rich can then undergo mass spectrometry analysis for isotopic composition. However, the relatively coarse SEM-AM analysis may not provide sufficient detail on individual particles or distinguish between natural and enriched uranium. A "confirm and characterise" step using SEM, EDS, and FIB-ToF-SIMS allows for secondary screening before LG-SIMS. This semi-non-destructive step provides detailed particle morphology and chemistry, as well as an indication of ^{235}U enrichment. By identifying particles with suspected isotopic anomalies, this step enhances the efficiency of LG-SIMS analyses.

The final step of the workflow follows conventional methods, where precision isotopic measurements are performed using an LG-SIMS instrument. The stage positions of previously identified particles enable targeted precision measurements. As these analyses are generally destructive, the operator can decide not to analyse a particle if sufficient information has already been obtained from FIB-ToF-SIMS.

When maximum sensitivity for man-modified uranium particles is required, and there is instrument availability, then the workflow can begin with LG-SIMS automated particle measurement (APM). SEM-AM and individual particle analysis can then be subsequently performed on material that has not be sputtered away by the LG-SIMS measurements.

4.1. Case study

The following describes the results from an analysis using this workflow. SEM-AM was used to scan a 25 mm diameter silicon wafer containing particles from a swipe sample. A bright-phase search routine targeted high atomic number particles, with a step size of 0.5 µm. The automated analysis completed in 29 minutes, identifying 109 particles that met the classification criteria for a uranium oxide phase. The identified uranium particles ranged in area from 1 µm² to 14 µm², with an average size of 3 µm². Figure 1 presents a BSE mosaic of the entire silicon wafer alongside a mosaic indicating the fields of view containing uranium particles. Figure 2 shows the particle size distribution and details of the ten largest particles, including their x-y stage coordinates.

The stage positions of uranium-bearing particles are then used to identify those of interest for detailed characterisation. Detailed SEM-EDS measurements on specific particles can be conducted either within the same instrument using a review function or in the FIB-ToF-SIMS instrument, utilising the stage mosaic and position list to locate the particles. High-magnification SEM imaging was used to analyse particle morphology (Fig. 3). Elemental composition was determined via EDS point spectra, providing semi-quantitative analysis (with accuracy limited by particle morphology and size). The results for ten particles are summaried in Table 1. Quantitative EDS results confirm the SEM-AM classification of a uranium oxide phase and indicate the presence of varying amounts of Fe, Na, and Al. Up to 25 wt% Si was detected, though it is assumed that most Si X-rays originated from the substrate.

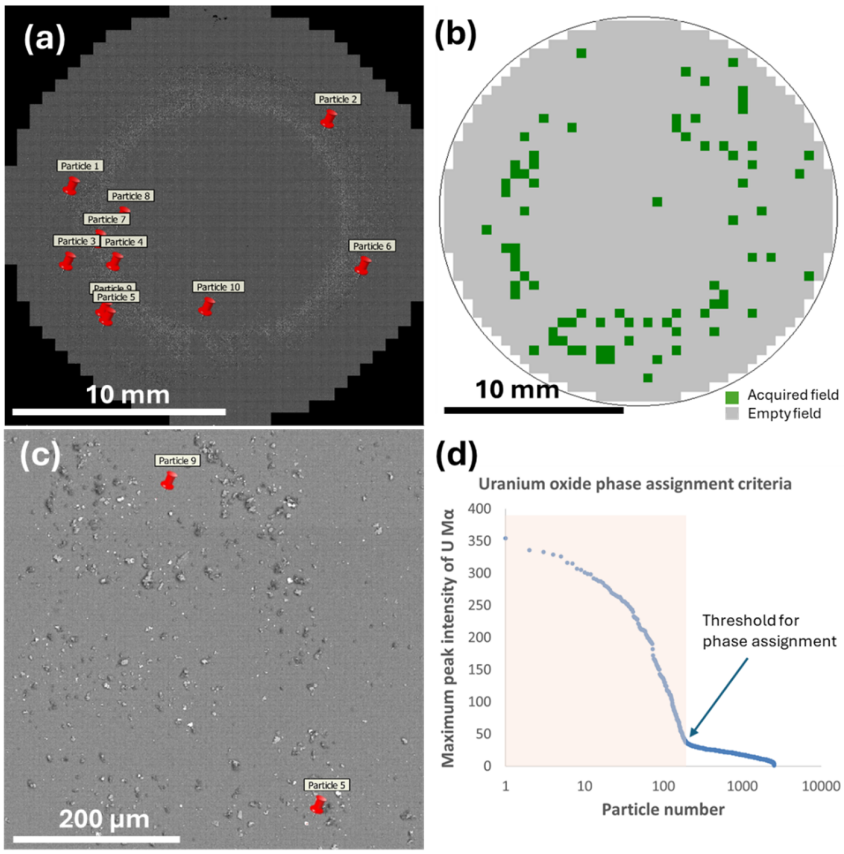
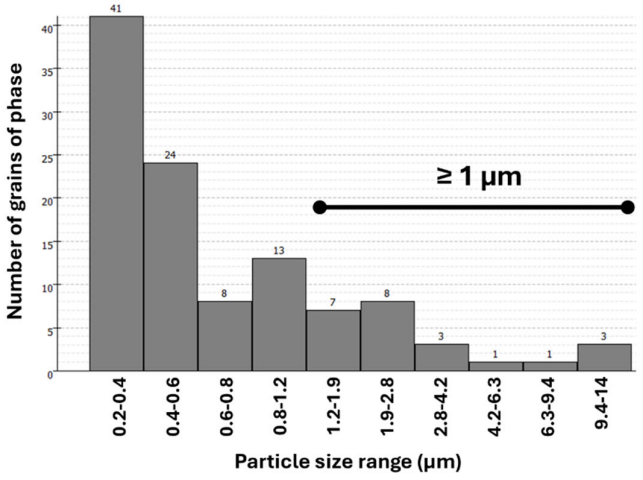


Figure 1. a) BSE mosaic from SEM-AM results with 10 uranium oxide particle positions identified. b) SEM-AM output indicating the fields where X-rays were acquired in the bright phase analysis routine. c) Enlarged portion of the mosaic showing locations of two particles. d) U-Mα X-ray intensity versus particle number plot to indicate where the threshold was determined for phase assignment as uranium oxide.



Grain	Area[px]	Surface[px]	Size[µm]	X[µm]	Y[µm]
1	54	28	4.1	-7676	593
2	49	24	3.9	4475	3855
3	37	29	3.4	-5635	-3084
4	34	30	3.3	-7861	-3065
5	18	12	2.4	-5973	-5754
6	12	9	2.0	-6440	-1980
7	10	7	1.8	-5292	-859
8	9	8	1.7	-2718	4961
9	9	7	1.7	3197	5722
10	9	9	1.7	1089	9968

Figure 2. Particle analysis results from SEM-AM analyses. Details of 10 grains/particles are displayed in the table on the right.

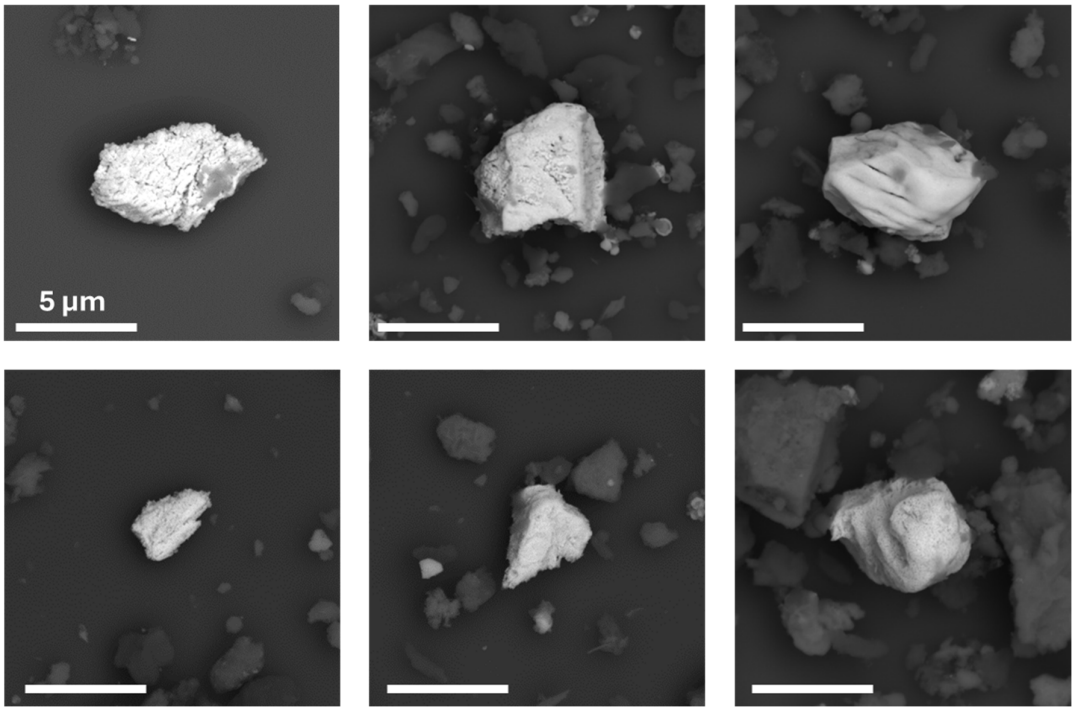


Figure 3. BSE images of detected uranium oxides particles with a variety of morphologies. Scale bar represents 5 µm.

Table 1. Semi-quantitative chemical analysis of particles by EDS (uncertainties are in brackets). Si signal is resultant an interaction volume that includes the substrate.

Particle number	Al (wt%)	Na (wt%)	Fe (wt%)	O (wt%)	Si (wt%)	U (wt%)
1	< 1 %	< 1 %	5.6 (0.3)	< 1 %	*2.8 (0.1)*	91.5 (4.6)
2	< 1 %	< 1 %	2.8 (0.1)	6.5 (0.3)	*1.4 (0.1)*	88.6 (4.4)
3	< 1 %	< 1 %	2.5 (0.1)	5.1 (0.3)	*1.4 (0.1)*	90.6 (4.5)
4	< 1 %	< 1 %	3.0 (0.1)	7.1 (0.4)	*9.8 (0.5)*	79.2 (4.0)
5	< 1 %	< 1 %	2.3 (0.1)	8.1 (0.4)	*24.7 (1.2)*	63.5 (3.2)
6	< 1 %	1.6 (0.1)	3.0 (0.2)	7.4 (0.4)	*10.8 (0.5)*	76.7 (3.8)
7	< 1 %	< 1 %	3.0 (0.1)	3.6 (0.2)	*4.6 (0.2)*	88.7 (4.4)
8	< 1 %	1.7 (0.1)	3.9 (0.2)	12.3 (0.6)	*3.9 (0.2)*	77.4 (3.9)
9	< 1 %	< 1 %	3.2 (0.2)	6.4 (0.3)	*6.7 (0.3)*	83.3 (4.2)
10	< 1 %	< 1 %	3.7 (0.2)	4.6 (0.2)	*8.5 (0.4)*	83.0 (4.2)

The isotopic composition of the particles was analysed using FIB-ToF-SIMS to assess any enrichment in ^{235}U. The time-of-flight technique generated a mass spectrum up to a mass-to-charge ratio of 340, containing peaks from primary ions (Ga), surface contaminants, other phases, and the particle of interest (Fig. 4). Uranium, uranium oxide, and uranium dioxide peaks were detected from the particle. The relative areas of the $^{235}U^{16}O_2$ and $^{238}U^{16}O_2$ peaks were used to determine ^{235}U enrichment as these has the highest signal intensity. Particles 4 and 10 exhibited enriched ^{235}U abundance (Table 2). However, uncertainties were significant due to the low signal-to-noise ratio for the minor isotope measurement. The FIB-ToF-SIMS analysis consumed only a small portion of each particle (Fig. 4), leaving sufficient material for subsequent precision isotopic analysis by LG-SIMS (results not shown here).

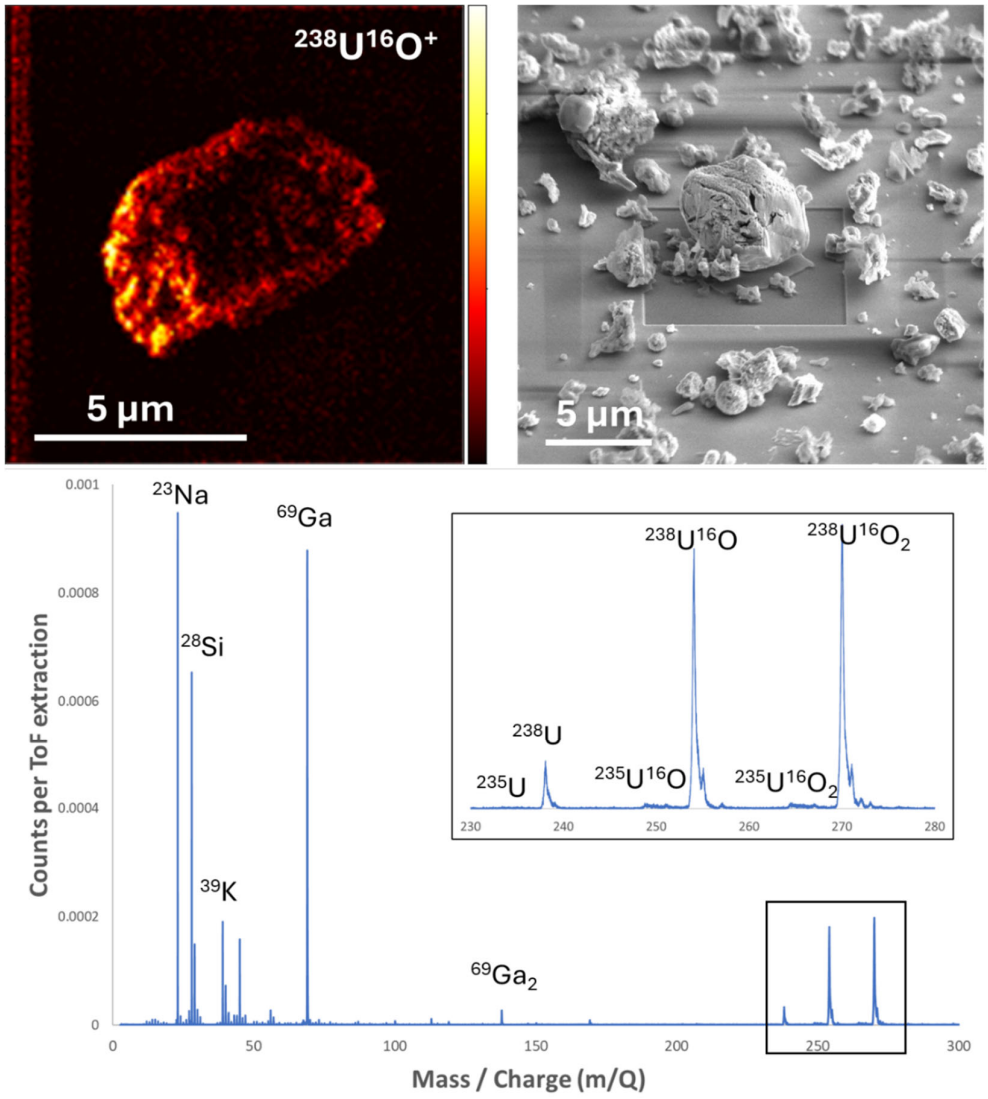


Figure 4. FIB-ToF-SIMS ion image and an SEM image of a particle after the analysis. A ToF-SIMS mass spectrum from a uranium oxide particle is also included.

Table 2. FIB-ToF-SIMS derived uranium isotopic ratios from two anomalous particles.

Particle number	Relative abundance of ^{235}U
4	2.7 ± 0.9 %
10	4.2 ± 1.1 %

5. CONCLUSIONS

This paper presents a workflow for the analysis of environmental monitoring filter samples using SEM-AM, FIB-ToF-SIMS, and LG-SIMS for the efficient identification and characterisation of uranium-bearing particles. The bright-phase automated search routine enabled the rapid identification of uranium particles on a planchet/Si wafer containing thousands of other phases. SEM-AM facilitates a high throughput of samples and provides the stage location information for subsequent analyses on particles of interest. The confirm and characterise step generates detailed information on particle morphology, elemental composition, and potential ^{235}U enrichment. This search and characterisation workflow not only optimises the use of LG-SIMS but also provides essential data for assessing the provenance of particles of interest. The combination of these techniques offers a comprehensive approach to detecting and characterising uranium-bearing particles in environmental monitoring samples. By integrating automated search, targeted characterisation, and precision isotopic measurements, this workflow improves analytical efficiency, minimises operator workload, and enhances the accuracy of uranium particle assessments. Future advancements in automated analysis and mass spectrometry resolution may further refine this workflow, making it even more effective for nuclear safeguards and environmental monitoring applications.

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