Rapid Gamma Screening of Shipments of Analytical Samples To Meet DOT Regulations

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ABSTRACT

The accelerated closure program at Rocky Flats required the capacity to ship up to 1000 analytical samples per week to off-site commercial laboratories, and to conduct such shipment within 24 hours of sample collection. During a period of near peak activity in the closure project, a regulatory change significantly increased the level of radionuclide data required for shipment of each package. In order to meet these dual challenges, a centralized and streamlined sample management program was developed which channeled analytical samples through a single, high-throughput radiological screening facility. This trailerized facility utilized high purity germanium (HPGe) gamma spectrometers to conduct screening measurements of entire packages of samples at once, greatly increasing throughput compared to previous methods. The *In Situ* Object Counting System (ISOCS) was employed to calibrate the HPGe systems to accommodate the widely varied sample matrices and packing configurations encountered. Optimum modeling and configurational parameters were determined. Accuracy of the measurements of grouped sample jars was confirmed with blind samples in multiple configurations. Levels of radionuclides not observable by gamma spectroscopy were calculated utilizing a spreadsheet program which can accommodate isotopic ratios for large numbers of different waste streams based upon acceptable knowledge. This program integrated all radionuclide data and output all information required for shipment, including the shipping class of the package.

SAMPLE MANAGEMENT STRATEGY

The US Department of Energy (DOE) and associated stakeholders have increasingly demanded tightly defined schedules for decontamination, environmental remediation and decommissioning of former nuclear weapons sites. Consequently, there is an urgent need for strategies that accelerate analytical processes necessary for characterization, while maintaining accuracy, precision and defensibility [1].

A single centralized and streamlined sample management system (summarized in Figure 1) was developed at the Rocky Flats site to avoid redundant activities and conflicting requirements and practices, while ensuring reliable tracking of the high number of samples and the data associated with them. In this strategy, the on-site analytical staff worked with the project teams and

sampling technicians from the start of the project by assisting in development of Sampling and Analysis Plan (SAP). Based on SAP requirements, the Project Lead generated a Sample Analysis Request Form (SARF) and a Chain of Custody (COC), providing specific details that instructed the sampling technicians on the desired sampling locations and schedule, and defining clear parameters for collection, storage, packaging and unique identification of the samples. For example, sample jar sizes and composition, hold times, and collection methods (i.e., coring, scraping, smears, etc) were set out in these forms. Importantly, the capacity of required off-site laboratories to analyze the samples in the desired time frame was confirmed at this time in order to avoid delays that would lead to exceeding the maximum hold times for collected samples.

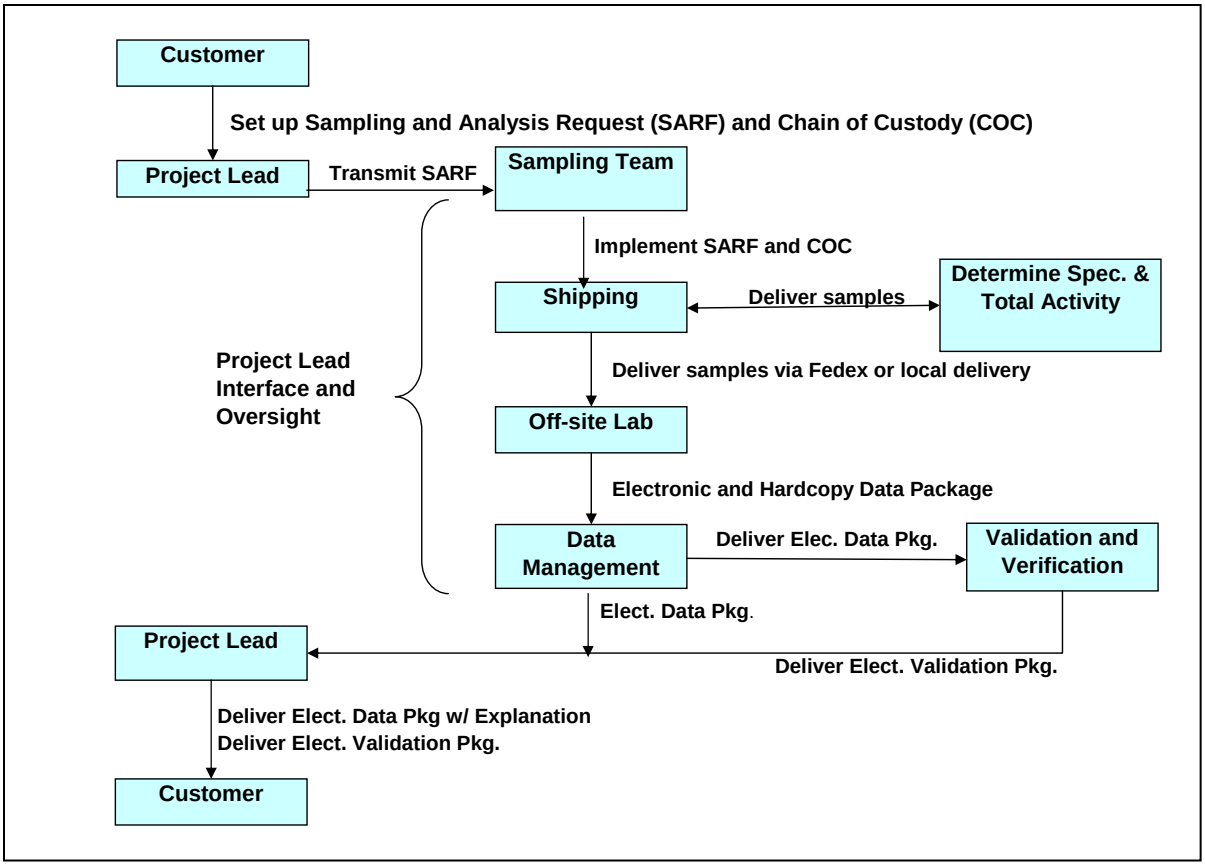

Figure 1. Process diagram of sample and data flow through the accelerated system.

Safety meetings and pre-evolutionary walkdowns were held with all project staff. Samples were then collected and transported in compliance with site traffic procedures to the receiving area of the high throughput radiological screening facility. At that location, a designated Shipping/Receiving Officer (SRO) verified the COC and inspected and documented the integrity of the samples. Specifically, it was the responsibility of the SRO to ensure that samples met the requirements specified in the SAP and other work control documents. For example, it was vital that documentation of contamination surveys of the sample jars and the intended shipping container – conducted at the sampling site – accompanied each sample. Only in this way could it be ensured that all shipping containers were free of internal and external contamination. Further,

it was verified that all samples had an on-contact dose rate of < 0.5 mrem/hr or as required by the corresponding work control document.

The packages of samples were then subjected to a screening by HPGe gamma spectroscopy utilizing the ISOCS / LabSOCS system, in order to comply with US Department of Transportation (DOT) regulations (see sections below).

Once the DOT compliance measurements had been made and the shipping class of the package determined, the samples were shipped to an off-site commercial laboratory for analysis. When analysis was completed, this laboratory provided an electronic and a hardcopy data package to the data management group of the sample management office (NOT directly to the requesting project lead), where the results were subjected to data validation and verification *before* being delivered to the project lead, along with an electronic data verification package.

COMPLIANCE WITH US DOT REGULATIONS

Prior to shipping on public roads or by air, radioactive material must be characterized in accordance with DOT regulations including 49 CFR 173. Previously, shipping in compliance with 49 CFR 173 did not require that the activities of *individual* radionuclides in a shipment be determined. However, the revised regulation effective October 1, 2004, defines exemption values for specific activity and total activity *for each individual radionuclide* in a shipment [2]. Therefore, the activities of each radionuclide in a shipment must now be reported.

Prior to this regulatory change, the preferred methods for DOT compliance measurements, often known as radscreens, favored sub-sampling followed by gross alpha/beta counting. However, such methods fail to provide individual radionuclide activity concentrations, and are therefore no longer compliant in most circumstances. Additionally, methods that involve sub-sampling create significant laboratory waste and require extensive radiological controls such as fume hoods and rigorous contamination control programs. In addition to adding expense, these are simply cumbersome within an accelerated closure program.

An ideal method for DOT radscreens would provide high throughput and rapid quantification of each radionuclide present, yet be non-intrusive and non-destructive, and generate no laboratory waste. A method was developed which meets each of these criteria by combining gamma spectroscopy with application of process knowledge-based scaling factors.

GAMMA SPECTROSCOPY STRATEGY

HPGe gamma spectroscopy was employed utilizing the *In Situ* Object Counting System (ISOCS) to measure up to 20 individual sample jars at a time within their shipping container. Conducting measurements within the shipping container allowed samples to be refrigerated (i.e., by ice packs) if necessary during measurement in order to maintain any unique storage requirements. Matrices included soils, dry chemicals, oils, sludges, water, dry chemicals, putative asbestos samples, paint chips, and concrete. Seven HPGe detectors were deployed in the trailerized facility in order to support the required throughput. Electrical generators supplied power after site electrical supplies were shut off as part of D&D operations.

The process was validated by a blind study in which sample bottles containing mixtures of Am-241, U-235, U-238 and other radionuclides were presented to the investigators as unknowns and measured in multiple configurations. Levels of radionuclides that do not emit gamma rays or which have gamma ray abundances too low to be directly observed were calculated from decay chain data and process knowledge using a customized spreadsheet, as described below.

Radiochemists from Kaiser-Hill at Rocky Flats prepared 23 sample bottles containing widely varying activity concentrations of U and Am dissolved in 1 N nitric acid and presented these as unknowns to the gamma spectroscopy group (Table I). These bottles were arranged into four different groups, and some or all of the bottles were used in each group.

The bottles were assembled into mock shipping packages which were analyzed by ISOCS / HPGe gamma spectroscopy seven times each: four times in configuration A in order to determine reproducibility, and once each in configurations B, C, and D to determine the effect of source distribution. Figure 2 shows an example of the configurations for a single sample set. The order of analyses was A-B-A-C-A-D-A, to require the operator to re-set the samples even between analyses of the same configuration. These configurations were chosen to represent the most likely arrangement of samples in the shipping container based upon bottle size and shape and were not random. Sample bottles were arranged with the bottoms of the bottles facing the detector (i.e., with their long axes parallel to the long axis of the HPGe detector), so that no bottles were blocked from the detector field of view by other bottles, and with the detector aimed at the center of the stack.

Am-241, U-235 and U-238 were selected for individual quantification and comparison since they represented the most prominent and directly measurable contaminants encountered at the Rocky Flats site. Site acceptable knowledge regarding the composition of Pu streams at Rocky Flats allowed -- in most cases -- the calculation of Pu isotopics directly from the Am-241 ingrowth. This greatly simplified sample analysis and reduced required count times. Am-241 was quantified from the 59.5 keV peak. U-235 was quantified primarily via the 143.8 keV peak in order to avoid interference from the 186.1 keV peak of Ra-226 (unavoidably present in the available materials used to mix the unknowns) with the more abundant 185.7 keV U-235 line. U-238 was quantified from the 1001 keV peak of Pa-234m and the 93 keV peak from Th-234, as these daughters could reliably be considered to be in isotopic equilibrium for the mixture provided.

Prior to measurement, the individual bottles were scanned with a survey instrument in order to identify particularly high radioactivity samples and to assist in ISOCS modeling of source distribution. The sample bottle configuration was then modeled using the ISOCS Complex Box template (see Figure 3 and text below), with effective atomic compositions programmed for the shipping container, sample bottles, and contents.

The packages were measured for 60 minutes in each configuration using a CANBERRA broad energy germanium (BEGe) detector with a beryllium window, 13% nominal relative efficiency and crystal size of 28 cm^2 by 20 mm thickness. It was interfaced to a CANBERRA InSpector multichannel analyzer and a PC. Spectra were collected and analyzed on CANBERRA Genie 2000 software running ProCount 2000 and Gamma Acquisition and Analysis packages.

Table I. Ranges of activity concentrations per bottle in unknown samples.

	Lowest Activity Concentration (pCi/g)	Highest Activity Concentration (pCi/g)
Am-241	0.9	21,000
U-235	1.06	34
U-238	206	736

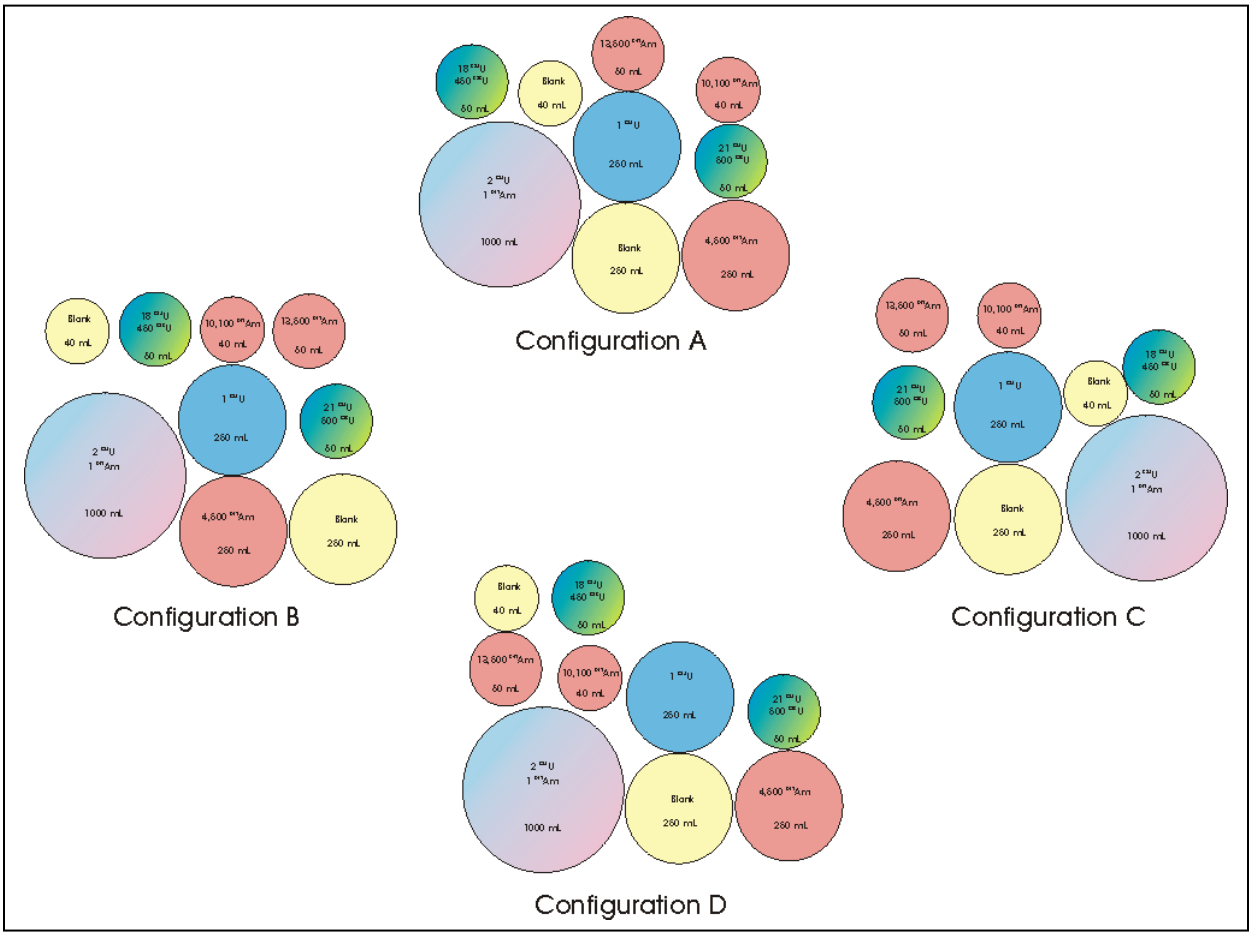

Figure 2. Configurations of sample bottles for Package 3 used in the HPGe /ISOCS validation study.

After completion of all counts and data analysis, the actual radionuclide concentrations for each blind sample bottle were revealed to the gamma spectroscopy group and the accepted value for each package was compared to the experimental data. Two types of comparisons were made. The first utilized data generated using ISOCS models (called "detailed") which took into account the distribution of relative activity over the sample configuration, based upon prior scanning of each individual sample jar with a survey meter. The relative activities were programmed into the

ISOCS model using the Concentrated Source and Source Layer utilities (see Figure 3). The second utilized data in which the ISOCS models (called "generic") contained no activity distribution data. Both types of models contained identical values for all other ISOCS parameters (i.e., matrix and container atomic compositions, bottle and shipping package wall thicknesses, dimensions, source-to-detector distance, etc). The purpose of this strategy was to estimate the degree of uncertainty contributed by source distribution, and to assess the efficacy of using a survey instrument scan to reduce that uncertainty. Results are reported in Table II.

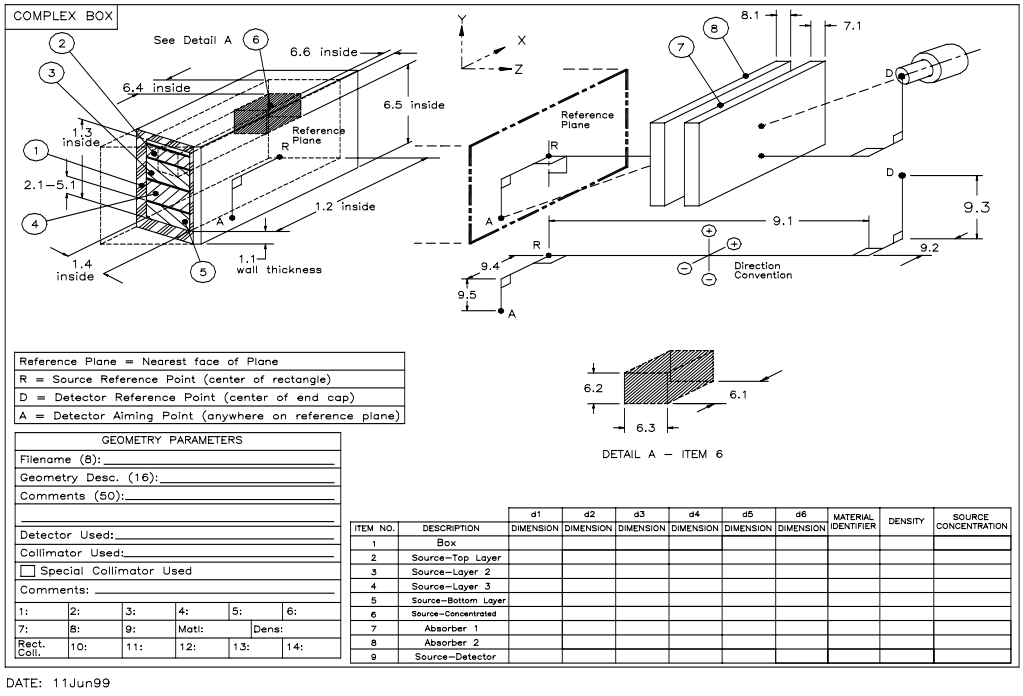

Figure 3. The ISOCS Complex Box template was used to input parameters for the measured packages, including locations of concentrated sources (see text).

These results demonstrate that when the source distribution is reasonably well known, the ISOCS HPGe gamma spectroscopy screening measurements are within 20% of the known values. They also confirm the contribution of source distribution to the uncertainty of the measurement, and they validate the usefulness of even survey instrument-level knowledge of that distribution in reducing the uncertainty. In general, heterogeneity of source distribution is the largest contributor to total uncertainty in non-destructive assay of radioactive materials [3].

Several important and instructive ISOCS modeling considerations were encountered during the performance of the study. The density value programmed into the ISOCS model for the matrices must take into account that bottles and contents do not fill the entire volume modeled – that is, the inside volume of the sample shipping package, which was in this case a polypropylene picnic-type cooler. Therefore, it is necessary to calculate an effective density from the sample mass (determined directly by weighing all of the samples) divided by the total volume of the shipping package. Likewise, it was necessary to calculate an effective material composition as a

weighted composite of the container material (i.e., polypropylene) and sample contents (i.e., water, soil, etc). An advantage of the ISOCS software was that refinement of the data in this way could be done by remodeling *without a recount*. Finally, the ISOCS model should be validated by confirming that calculated efficiency curve is valid over wide range of energies. This is possible where two or more widely spaced peaks are known to represent the same quantity (i.e., the 93 keV Th-234 peak and the 1001 keV peak of Pa-234m in this study).

Table II. Comparison of Mean Percent Error of Generic vs. Detailed ISOCS Models of Each Package

	Mean Percent Error[a]							
	Package 1		Package 2		Package 3		Package 4	
	Generic[b]	Detailed[c]	Generic[b]	Detailed[c]	Generic[b]	Detailed[c]	Generic[b]	Detailed[c]
Am-241	20.7	18.8	14.3	-15.9	-31.8	-6.3	57.6	-4.1
U-235	-18.0	-6.3	34.9	8.3	-34.6	-13.3	-57.1	18.3
U-238	-17.5	-17.1	25.9	18.0	-24.1	8.2	-47.4	1.2
Reported total activity[d]	19.1	17.3	14.5	-15.1	-31.7	-6.1	38.6	-3.0

[a] Mean Percent Error = ((Known – Observed) / Known) * 100

[b] Generic ISOCS models had no information about relative activity of individual bottles.

[c] For detailed ISOCS models, individual bottles were pre-scanned using a survey meter to allow approximate assignment of the fraction of total activity to the layer and/or concentrated source parameter.

[d] Not additive with the individual radionuclide percent error values since widely varying activity concentrations of the radionuclides were used. See Table 1 for range.

APPLICATION OF PROCESS KNOWLEDGE FOR FINAL DOT SHIPMENT DATA

In practice, not all radionuclides in a shipment can be expected to be readily analyzable by HPGe gamma spectroscopy. For example, Pu isotopes tend to have gamma ray abundances on the order of 10^{-5} γ/disintegration or lower and thus emit gamma rays at least 10,000 times less intensely than the readily observable Am-241, which emits approximately 0.36 γ/disintegration [4]. Further, common contaminants at former nuclear weapons facilities such as Sr-90 and tritium emit no gamma rays at all. In these cases, it is highly useful to apply scaling factors that relate the levels of observable radionuclides to those that are not observable, based upon validated process knowledge.

At Rocky Flats, a spreadsheet program was created that calculated the activity concentrations and total activities of non-observable radionuclides based upon process knowledge and decay chain data for that waste stream. While the fact that most material at Rocky Flats was of the same age and composition simplified this process, the spreadsheet program was designed to accommodate a large number of independent isotopic compositions and waste streams. By

working closely with site radiological engineers and waste classifiers, new waste streams may be characterized and added to the database relatively easily.

The spreadsheet program then compared the quantitative data for each individual radionuclide to its appropriate A_2 value from 49 CFR 173.435 and exempt quantity level from 49 CFR 173.436. Finally, it generated a printout of all relevant DOT shipping data. An example of such a printout is shown in Figure 4. The "Evaluation for Shipment" field would show "Exempt", "Limited Quantity", "Type A", or "Exceeds Type A" based upon these data.

Sample IDs:									
Matrix (liquid / solid):		**Solid**							
Shipment Net Wt. (grams):		**1509922.00**							
Evaluation for Shipment:									
	Total Average Activity (Ci/g)	**Shipment Total Activity (Ci)**	**Exempt Activity (sum of fractions)**	**Exempt Conc. (sum of fractions)**	**Limited Quantity (sum of fractions)**	**LSA (sum of fractions)**	**Type A (sum of fractions)**	**Total Fissile Gram Equivalent**	**Total Gram Equivalent**
								n/a	
A	B	C	D	E	F	G	H	I	J
Isotope	**Total Shipment Activity Conc. by Isotope (Ci/g)**	**Total Shipment Activity by Isotope (Ci)**	**Exempt Activity (fraction of maximum by isotope)**	**Exempt Conc. (fraction of maximum by isotope)**	**Limited Quantity -- Solids (fraction of max. activity by isotope)**	**LSA -- Solids (fraction of maximum conc. by isotope)**	**Type A -- Solids (fraction of maximum activity by isotope)**	**Calculated Fissile Gram Equivalent by Isotope (grams)**	**Isotopic Gram Equivalent by Isotope (grams)**
Am - 241									
Pu - 238									
Pu - 239									
Pu - 240									
Pu - 241									
Pu - 242									
Ra - 226									
Ac - 228									
Th - 230									
Th - 231									
Th - 234									
Pa - 234 m									
K - 40									
Co - 57									
Co - 60									
Cs - 137									
Cm - 243									
Am - 243									
Cm - 244									
Np - 237									
U - 238									
U - 236									
U - 235									
U - 234									
U - 233									
H - 3									

Figure 4. DOT shipping printout sheet.

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