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Dissolved Gas Analysis (DGA) by EPRI Disposable Oil Sampling System (EDOSS)

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TR-111322

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REPORT SUMMARY

The utility industry has increasingly applied dissolved gas analysis (DGA) to assess the condition of fluid-filled equipment. Modifications to the EPRI Pressurized Oil Sampling System (EPOSS), a novel DGA method developed in 1983, have rendered the system more cost-effective without compromising its accuracy and precision. Designated the EPRI Disposable Oil Sampling System, EDOSS safely operates with all types of fluid-filled equipment under most weather conditions.

Background

While EPOSS continues to serve the industry well, the time required to assemble, disassemble, and clean the cells adds to the cost of the analysis. In addition the cells are large, heavy, and expensive, with a shipping container for 20 EPOSS cells weighing about 60 lbs. This adds to the cost of overnight air freight. A chlorinated solvent used to clean the cells also poses environmental concerns. EPRI undertook the challenge of enhancing the cost-effectiveness and environmental safety of the EPOSS method.

Objectives

To design an easy-to use, inexpensive, but equally accurate version of EPOSS, using a disposable glass vial for fluid collection and analysis as well as a commercially available headspace analyzer to automate analysis.

Approach

Investigators divided the project into four tasks. First, they developed a disposable crimp-top glass vial able to hold its vacuum for about three weeks, with emphasis on selection of a proper rubber stopper with low permeability. Second, to facilitate fluid sampling, they developed a quick-disconnect coupler and a suitable adapter for holding the needle, making fluid collection in the disposal crimp-top vial possible. Next, they installed a micro-pressure pump to promote sample collection. Finally, they described the theory of the headspace analyzer and compared DGA data generated by EDOSS and EPOSS systems under field conditions.

Results

EPRI has developed and tested a viable alternative to EPOSS under field conditions. The new system, EDOSS, can be employed for all types of fluid-filled equipment. Using the EDOSS system, investigators place a small volume of fluid in a disposable crimp-

top vial evacuated to an appropriate vacuum level. (Tests performed on these vials indicated that this vacuum level can be maintained for about 20 days.) As the fluid is admitted into the sealed EDOSS vial, dissolved gases rapidly evolve from the fluid until equilibrium is achieved between gases in the liquid and the headspace. The evolved gases remain confined in the glass vial until analysis is complete. The micro-pressurization system facilitates the sampling of high-viscosity fluids used in extruded cable terminations and is also suitable for low-pressure self-contained cables. Investigators perform gas analysis in the same vial, which now becomes the extraction vessel. As a result, this method provides a simple DGA procedure with no subsequent liquid handling during gas extraction and analysis. The DGA procedure also permits analysis of up to 50 vials at one time. The theory behind this method is identical to the EPOSS method, with the additional advantage of using inexpensive disposable vials.

This report describes all ancillary equipment needed for cell preparation and field sampling. It also provides details for the modification of a commercially available headspace analyzer so that it can be installed in tandem with two gas chromatographs to cover a large number of gases. Finally, the report discusses analysis accuracy and precision and compares the EDOSS analysis with the established EPOSS procedure.

EPRI Perspective

Fluid-filled equipment—which includes transformers, cables, bushings, terminations, and circuit breakers—is an integral part of the electrical system. Because this diverse equipment represents considerable utility investment and a high proportion of it is advancing in age, proper periodic maintenance is essential. EDOSS offers a cost-effective system for using DGA techniques to assess the condition of fluid-filled equipment. This research demonstrates that the EDOSS system represents a viable alternative to EPOSS, while offering significant cost and handling advantages. Related EPRI work includes Dissolved Gas Analysis Method for HPFF Paper Cable (EL-7488-L) and Behavior of Paper-Polypropylene-Paper Laminate Under Thermal and Electrical Stresses (TR-111321).

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ABSTRACT

A new approach for Dissolved Gas Analysis (DGA) is presented. This novel method resulted from modifications of the previous EPOSS (EPRI Pressurized Oil Sampling System) technique. These modifications were sought to render the EPOSS system more cost-effective without compromising its accuracy and precision. This was accomplished through an inexpensive sampling cell and reduction in cleaning, assembling and disassembling steps involved in the EPOSS approach. The new system, designated as EDOSS (EPRI Disposable Oil Sampling System, utilizes a disposable crimp-top vial for fluid sample collection and subsequent analysis by means of a commercially available headspace analyzer for automated analysis. The new system has the capacity to automatically analyze 50 samples, a significant increase over the 10-sample capacity of the currently available EPOSS system at Detroit Edison.

A relatively small volume of sample fluid (under 5 cc) is required for analysis in the EDOSS method compared to 20 cc for its EPOSS counterpart. All ancillary equipment needed for cell preparation and field sampling is presented. Details are also given for the modification of a commercially available headspace analyzer so that it can be installed in tandem with two gas chromatographs to cover a large number of gases. The new sampling glass cell is sealed with a disposable rubber stopper. The fluid sample is introduced by piercing the stopper with a hollow narrow needle. A fluid-sampling pressurization pump is described to sample equipment in which high viscosity fluids are employed at low pressures, as is true for extruded cable terminations. Information on analysis accuracy and precision as well as comparison with the already established EPOSS procedure is given in this report.

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INTRODUCTION

Fluid-filled equipment, which includes transformers, cables, bushings, terminations and circuit breakers, is an integral part of the electrical system. This diverse equipment represents considerable utility investment and, a high proportion of it, is advancing in age. About 30% of the high pressure fluid-filled transmission cable systems, the predominant form of U. S. underground transmission, are over 25 years old. Likewise, about 35% of the power transformers are over 30 years old. The rapidly emerging utility business climate dictates that efficient use of such assets should be made. This calls for proper periodic maintenance. The assessment of the condition of fluid-filled equipment through traditional evaluations of a fluid sample (dielectric breakdown, dissipation factor and color, etc.) has been made since the introduction of such equipment. This does not lead to reliable results for in-service fluids, although these tests are most appropriate for the selection and evaluation of new dielectric fluids. To enhance the value of periodic fluid testing, newer tests such as Dissolved Gas Analysis (DGA) and furfural content have been increasingly applied to fluid-filled equipment, with promising results.

Under EPRI sponsorship dating back to 1983, Detroit Edison has been primarily involved in the development of the emerging DGA technology for fluid-filled transmission cables. A cardinal feature of this effort had been the development of a novel DGA method, referred to as EPOSS (EPRI Pressurized Oil Sampling System). This method is based on headspace analysis and the details are described in a licensable EPRI report[1.] In the EPOSS approach, both the fluid sampling and analysis are performed in the same vial, leading to reduced sample manipulation and consequent enhanced accuracy and precision. The changes occurring in gas concentrations in the fluid-filled equipment over short spans of time are generally small under most conditions. This can be true even for some severe cases, underscoring the importance of accurate sampling and analysis.

The EPOSS system has been applied to generate over 6,000 field data points since 1986, and is considered to have resulted in the largest DGA cable data bank in the world, let alone extensive laboratory data generation. Some of the results have been presented in an ESEERCO (Empire State Electric Energy Research Corporation) Report[2], 3 technical publications[345]and 3 EPRI INNOVATORS[678] the latter describe the successes achieved in identifying impending problems at 3 U. S. utilities. The advantages of the EPOSS method include:

- both sampling and analysis are performed in the same vial
- ease of application
- lends to automation
- no bubble formation, which occurs in syringes and steel cylinders
- environmental acceptability due to absence of mercury (associated with ASTM 3612)
- application to fluid samples with a wide range of gas content, often encountered
- suitability for a wide range of fluid viscosities utilized in various types of fluid-filled equipment
- long sample storage (25 days)
- elimination of human error through automation
- improved accuracy and precision

While the EPOSS system continues to serve the industry well, the time required to assemble, disassemble and clean the cells, despite an efficient cleaning system involving a vapor degreaser, adds to the cost of analysis. In addition, the cells are large (3 in. x 11 in.), heavy (~1,000 g) and expensive (~$450). A shipping container for 20 EPOSS cells weighs about 60 lbs. This adds to the cost of overnight air-freight. A chlorinated solvent (1,1,1 trichloroethane) is utilized to clean the used cells. This solvent poses environmental concerns.

Against this background, a new DGA method that retains all the positive features of the EPOSS system, while eliminating its shortcomings, has been developed. Unlike the EPOSS method, this new approach utilizes a small glass disposable vial, and hence the name EDOSS (EPRI Disposable Oil Sampling System).

The key challenges for the successful development of such a viable field-worthy method included:

- the development of a vial that can maintain appropriate vacuum (below 20 millitorrs) for about 20 days
- ability to introduce the fluid through a suitable rubber stopper with a narrow stainless hollow needle
- ability of the rubber stopper to promptly re-seal the pierced hole made by the needle as it is removed in both summer and winter temperature conditions

- the development of a suitable adapter incorporating the needle and a quick-disconnect coupler holding the crimp-top vial for needle penetration required for fluid sampling
- the development of a system to evacuate the disposable vial before the stopper is secured and crimped
- the development of a mini-pressurization pump to sample equipment containing highly viscous fluids at low pressures (for instance, extruded transmission cable terminations), and low pressure self-contained cable systems

To meet the above challenges, the project has been divided into 4 tasks. The collective objective of these tasks is to design an easy-to-use, inexpensive but equally accurate version of EPOSS, wherein the disposable glass vial serves the dual function of fluid collection and subsequent analysis. At the same time, this version (EDOSS) has to be fully capable of operating in field conditions on a consistent basis, with all types of fluid-filled equipment and weather.

Each task is briefly described below:

The Sampling Vial

The task relates to the development of a disposable crimp-top glass vial that is able to hold its vacuum for about 3 weeks. The selection of a proper rubber stopper with low permeability is crucial to maintain the required vacuum level in the vial. In addition, the stopper material has to be resilient enough to reseal as the needle is removed. This task discusses the choice of various stopper materials and designs.

Fluid Sampling for Typical Fluid-Filled Equipment

This task pertains to fluid sampling, the development of a quick-disconnect coupler and a suitable adapter holding the needle, making the fluid collection in the disposable crimp-top glass vial possible. The quick-disconnect coupler holds the vial as it is inserted into the adapter housing for needle penetration. The adapter incorporating the needle is attached to the sampling port. A 3-way valve is provided to allow for fluid flush before sampling. For transformers and fluid-filled cables, the fluid pressure is sufficient to force the fluid through the hollow narrow needle without any external aid.

Fluid Sampling for Fluid-Filled Equipment with High Viscosity Fluids at Low Pressure

Of all fluid-filled equipment, the extruded cable terminations have the highest viscosity fluids. The pressure head is not sufficient to force this viscous fluid through the hollow narrow needle. This task describes a micro-pressure pump to facilitate sample collection. The pump is installed between the sampling port and the crimp-top vial.

Validation of the EDOSS System

This task describes the theory of headspace analysis and compares DGA data generated both by EDOSS and EPOSS systems under field conditions. The results demonstrate that EDOSS compares favorably with EPOSS.

Conclusions

A viable alternative to EPOSS has been developed and successfully tested in field conditions. The new system is referred to as EDOSS and it can be employed for all types of fluid-filled equipment. This new system offers significant cost and handling advantages. To allow direct sampling of the fluid into the disposable vials, several components were designed, fabricated and successfully tested. A micro pressurization system was assembled to facilitate the sampling of high viscosity fluids used in extruded cable terminations. It is also suitable for low pressure self-contained cables. The analysis of a large number of dissolved gases was accomplished through a modified automated headspace analyzer and two gas chromatographs.

2

DESCRIPTION OF SAMPLING VIAL

The sampling vial utilized in the new EDOSS system consists of a 22 mm x 75 mm disposable crimp-top vial with a nominal capacity of 20 cc. This size is suitable for use with an auto-sampler associated with a headspace analyzer. The vial is closed with a rubber stopper and an aluminum crimp cap. The rubber stopper should have a low gas permeability, good resilience and compatibility with hydrocarbon fluids. The most important aspect of the stopper is its low gas permeability. This characteristic determines the period of time that the vial can maintain a proper vacuum. This level of vacuum assures a minimal concentration of oxygen and nitrogen. After sampling, the stopper has to be able to contain the gases until the analysis is performed.

The time lag for gas diffusion through a rubbery material can be estimated from[9]

$$\theta = \frac{l^2}{6D} \qquad \text{(eq. 2-1)}$$

where θ is the time lag; l, the membrane thickness; and D, the gas diffusivity. While the nature of the material can be selected to minimize the value of D, the design can have a greater impact by an increase in the stopper thickness (l).

Elastomeric materials with low gas permeability include: butyl rubbers, fluoro-elastomers and polyacrylics. Rubbers composed of 100% halobutyl rubber have very low gas permeability. Among these, 100% bromobutyl rubber is utilized in the inner lining of high quality car tires and most truck tires[10]

Rubber stoppers for crimp-top cells are available in various materials. A large number of these cells were tested to identify those with the lowest gas permeability characteristics, refer to Table 1. This table shows that the halobutyl rubber and the polyacrylic stoppers showed the lowest gas permeation. Polyacrylic stoppers were preferred in the beginning, until it was observed that under cold weather conditions this material became less resilient than the halobutyl rubber and small leaks were observed after pulling the needle away from the stopper at the end of the sampling

Table 2-1
Air Permeation into a Vial After 8 Days Sealed with Selected Stoppers

Stopper Material	Wall Thickness (mils)	Oxygen (ppm)	Nitrogen (ppm)	C. Dioxide (ppm)	Total (ppm)
Silicone (Supplier 1)	160	32,467 32,603 31,129	117,664 119,362 109,231	323 324 319	150,454 152,289 140,679
Neoprene (Supplier 1)	160	136 172 128	1,468 1,520 1,229	85 84 81	1,679 1,776 1,438
Butyl (Supplier 1)	160	333 329 358	1,451 1,195 1,494	13 14 12	1,797 1,538 1,864
Halobutyl (Supplier 3)	120	140 141 127	765 766 767	17 16 16	919 923 910
Butyl Rubber (Supplier 2)	160	229 185	1,092 978	2 8	1,323 1,171
Polyacrylic (Supplier 2)	160	95 101	541 665	12 13	648 779
Neoprene (Supplier 2)	160	234 175	1,311 1,040	35 33	1,580 1,248
Viton (Supplier 2)	160	279 184	1,290 816	13 11	1,582 1,011

process. In general, all stoppers have the same thickness of about 160 mils, except the halobutyl rubber ones. The halobutyl rubber stopper is characterized by a thickness of 120 mils. Despite the thinner wall of the halobutyl stopper, this material outperforms all other elastomers tested on the basis of per unit wall thickness. Although the level of gas leakage is small for the halobutyl rubber stopper, a thicker wall would decrease the leakage considerably as shown by eq. 2-1.

After the fluid sample is taken, it is recommended to maintain the cells upside down. Since the gas concentration of low molecular weight components in the liquid phase is considerably lower than the corresponding concentration in the gas phase, the possible migration of gases out of the vial is further reduced when the fluid is in contact with the stopper instead of the gas.

3

FLUID SAMPLING FOR TYPICAL FLUID-FILLED EQUIPMENT

The importance of correct sampling from fluid-filled equipment cannot be overemphasized. Subsequent handling, transport and longer storage, if needed, are equally important. Exposure of the fluid sample to the atmosphere leads to contamination by oxygen and nitrogen, including the escape of hydrogen and other light gases with high mobility and low fluid solubility characteristics. The key components of the sampling system are:

Sampling Vial

The disposable sampling vial has been described in Section 2.

Vial Evacuation Device

Before the disposable vial is used, it has to be evacuated, sealed with the stopper, and crimped. To accomplish this operation, the unit presented in Figure 1 was devised. In this figure, A corresponds to the 20 cc disposable glass vial; B is an o-ring seal; C is the vacuum manifold; D is the rubber stopper; E is the vacuum lever and F is the vacuum port connection. A vacuum gauge is installed on a T-fitting between the port F and the vacuum pump. After the appropriate vacuum is achieved, the lever (E) is actuated and the vials are pushed against the rubber stopper. After the vials are sealed with the stopper, the vacuum in the aluminum block is relieved and the vials are pulled out of the block. The vacuum inside the vials maintains the rubber stopper in place before the aluminum crimp is applied. The vials are labeled by scribing on the glass surface and are ready to be shipped. Long-term testing has proved that a good level of vacuum can be maintained for about 20 days. This time is at least double the time typically required to sample and ship back 50 samples to the EPRI Laboratories at Detroit Edison.

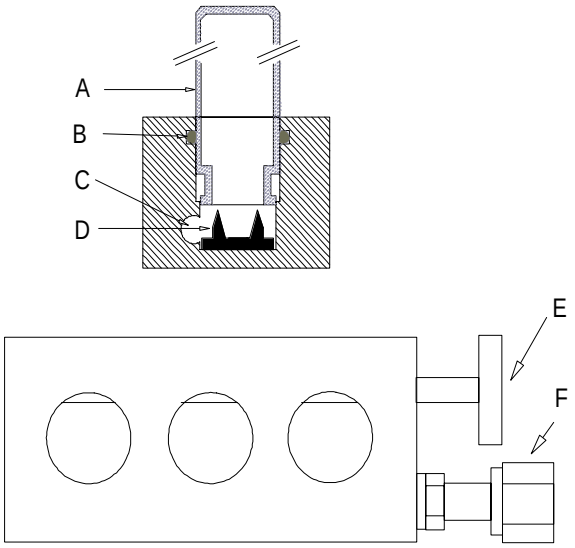

Figure 1 Schematic diagram of the evacuation system for EDOSS vials

Sampling Unit Assembly

A schematic diagram of the sampling unit and layout for the sampling of fluid-filled equipment are shown respectively in figures 2 and 3. The unit consists of a quick-disconnect coupler (B in Figure 2) modified to hold the disposable crimped-top vial (A in Figure 2), a suitable adapter incorporating the hollow needle while protecting it in a housing (C in figure 2), and finally a 3-way valve to allow fluid flushing before sampling, refer to Figure 3. O-ring sealed, zero clearance fittings were always utilized. These fittings have excellent performance in high vacuum and high-pressure applications and are easy to dismantle.

A 2" long, commercially available 21 gauge hollow stainless steel needle was soldered to the base of the adapter at the center of the protective housing (C in Figure 2). A 230-micron on-line filter can be installed before the 3-way valve to avoid needle obstructions from any debris in the fluid sample, as shown in Figure 3.

An additional rubber septum was installed in a small well incorporated in the quick-disconnect coupler holding the EDOSS vial. This septum must be compressed against the face of the crimped stopper to provide an additional seal while the needle is retrieved after sampling. The re-sealing of the rubber stopper after pulling the needle out is not instantaneous and the septum helps keep air off the vial as the rubber re-seals itself.

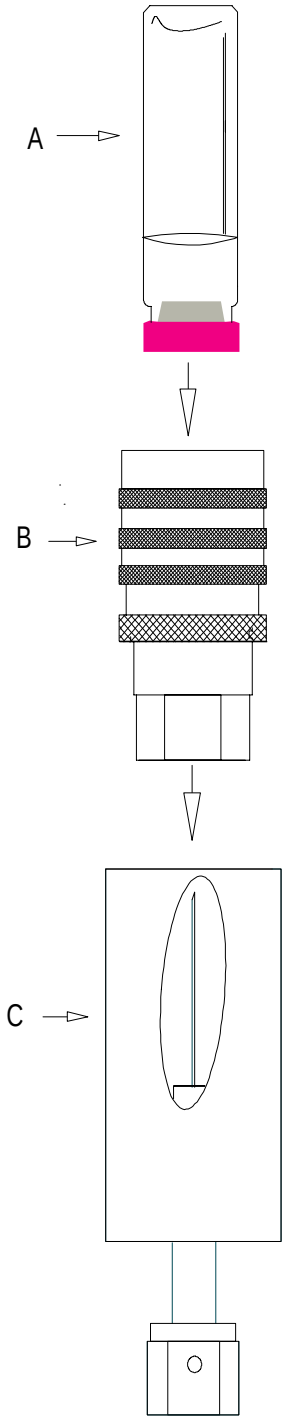

Figure 2 Schematic diagram of EDOSS sampling unit assembly

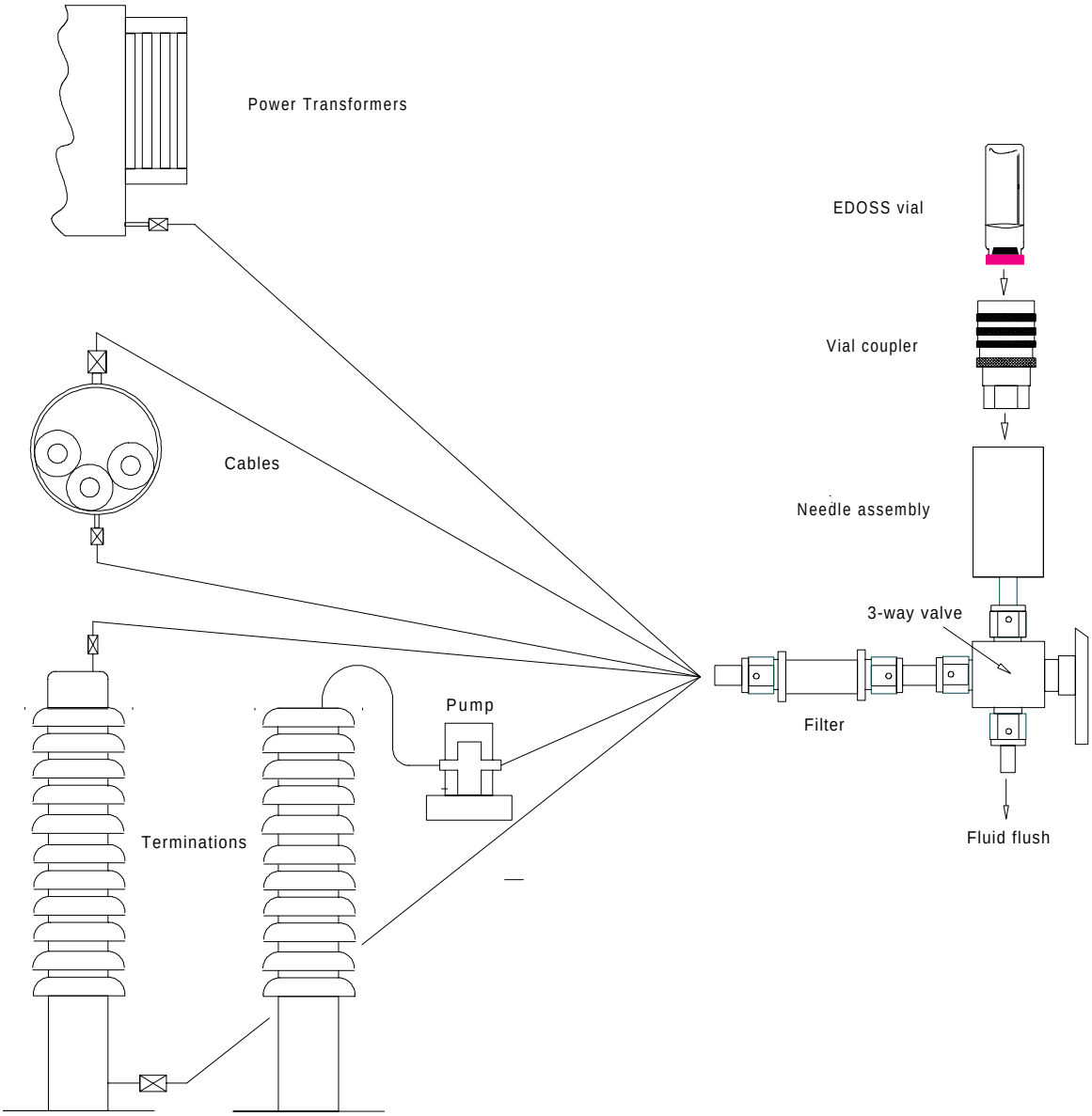

Figure 3 Schematic layout for the sampling of fluid-filled equipment with EDOSS

4

FLUID SAMPLING FOR FLUID FILLED EQUIPMENT WITH HIGHLY VISCOUS FLUIDS AT LOW PRESSURES

Equipment filled with high viscosity fluids and operating at low hydrostatic pressures cannot be sampled directly. The pressure head is too low to force the fluid through the hollow narrow needle. In such cases, a micro pressurization system must be installed before the needle. This pump would suction the fluid out of the fluid-filled equipment and force the fluid through the narrow needle into the disposable sampling vial.

After a careful review of available micro pumps, a reciprocating valveless pump was selected and tested both in the laboratory and field. It can be adjusted to deliver flow rates ranging from zero to 100%. The direction of the flow can also be reversed. The only difficulty encountered with this pump was the speed of the piston stroke. When pumping high viscosity fluids (3000 SUS or more) with a fast moving piston, even at the lowest stoke length setting, a very high pressure was generated at the piston head. This caused the motor belt drive to slip. This was overcome by modifying the diameter of the pulleys.

This setup was tested in low-pressure SCLF (self-contained liquid filled) cables as well as extruded cable terminations. While the dielectric fluid of SCLF cables has a low viscosity, its pressure is often low, depending on the cable type and location. Several Joslyn terminations containing high viscosity polydimethyl siloxane fluids were successfully sampled for DGA by EDOSS; the DGA results are given in tables 4-1 and 4-2. Whereas the former table refers to field data, the latter relates to laboratory work. The significance of these results will be discussed in a forthcoming EPRI report dealing with the application of DGA to extruded cable terminations. These tables are meant to illustrate that the EDOSS method can be readily applied to extruded cable terminations.

Table 4-1
Field DGA Data for a 138 kV Extruded Cable Termination by EDOSS

	South Termination			North Termination	
Gases	Phase A	Phase B	Phase C	Phase B	Phase C
Methane	11,737	219,309	12,617	223	372
Ethane	36	23	37	27	40
Ethylene	3.3	5.3	3.6	5.2	4.0
Acetylene	0	0	0	0	0
Propane	211	137	227	158	238
Propylene	7	6	8	5	10
Isobutane	1,283	768	1,301	884	1,345
n-Butane	864	544	951	763	1,017
t-2-Butene	24	11	23	14	26
1-Butene	236	115	232	165	241
Isobutylene	2,275	844	1,534	1,142	1,518
Hydrogen	13	18	17	32	25
C. Monoxide	405	209	232	342	686
C. Dioxide	7,546	11,709	8,646	4,837	6,609
Oxygen	13,054	13,736	14,549	69,617	17,533
Nitrogen	106,824	162,206	105,649	969,300	186,879

Table 4-2
Laboratory DGA Data for a 138 kV Extruded Cable Termination at Various Locations Within the Termination after Load Cycle Testing, refer to Figure 4.

	North Termination					South Termination	
Gases (ppm)	Headspace	Fluid Surface	Inner-Bottom	Outer-Bottom	Inner-center	Inner-Middle	Outer-Middle
Methane	9,867	13,470	12,118	8,112	15,593	9,874	10,284
Ethane	173	901	814	568	931	690	746
Ethylene	2	6	6	7	7	7	5
Acetylene	0	0	0	0	0	0	0
Propane	21	316	295	216	325	261	279
Propylene	1	20	18	15	20	16	17
Isobutane	16	443	428	327	458	383	406
n-Butane	12	482	481	342	506	385	404
t-2-Butylene	0	20	22	11	21	0	22
1-Butene	7	251	249	166	264	166	156
Isobutylene	55	1,938	1,897	1,371	2,023	2,110	2,295
Hydrogen	206	8	24	25	45	10	12
C. Monoxide	1,563	154	180	160	259	250	290
C. Dioxide	3,616	5,228	6,377	3,089	4,726	2,580	2,513

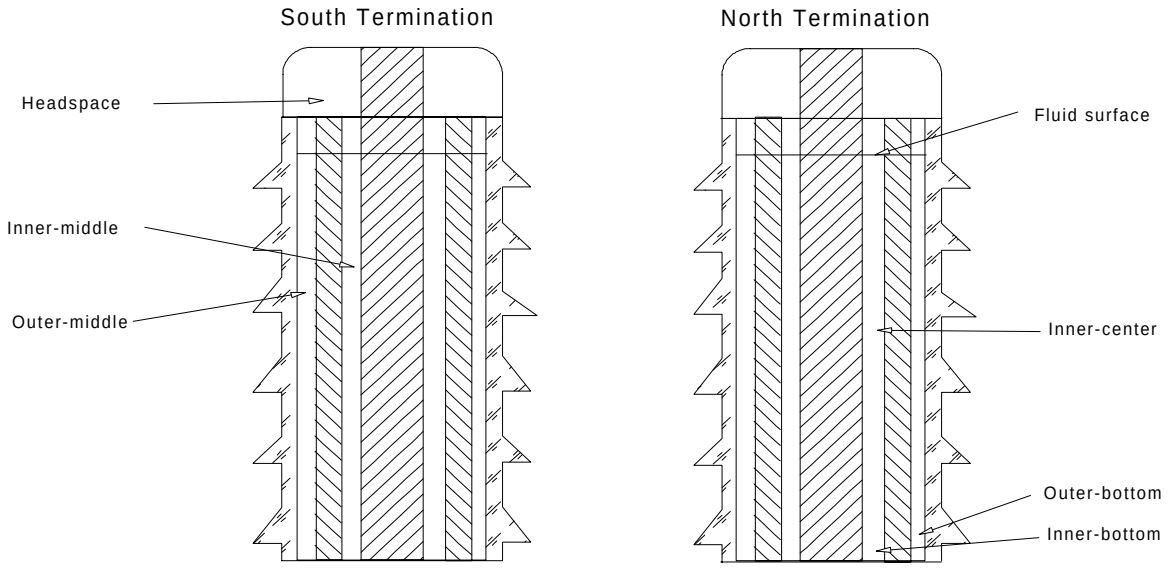

Figure 4 Sampling locations for a Joslyn 138 kV extruded cable termination by EDOSS

Because of the nature of Joslyn termination design, which has been extensively employed since the early 1970s, it is not possible to incorporate a sampling port at the bottom. The sampling for this termination design was performed by means of a 1/4 " OD flexible plastic tubing, connected to one side of the pump, with the EDOSS sampling device connected at the other end. Since the flow direction in this pump is reversible, both inlet and outlet ports are interchangeable. The free end of the 1/4 " OD flexible tubing was gently forced as far as possible in-between the cable insulation and the internal spacers or between the spacers and the inside wall of the ceramic housing. In some cases, it was possible to reach the top end of the stress cone.

Once the plastic tubing is installed, the fluid can be brought to the pump by the suction of the piston and then forced through the hollow needle into the EDOSS vial. After the necessary samples are taken, the pump flow can be reversed and the excess fluid pushed back into the termination.

It should be added that this pump can be readily connected to other extruded cable terminations with provision for a sampling port. The low sample volume requirement (5 cc) together with the ability to place the unused fluid back into the termination makes the EDOSS system the only available option to sample extruded cable terminations which contain a small volume of dielectric fluid.

5

VALIDATION OF THE EDOSS SYSTEM

In the EDOSS method, a small volume of fluid (~5 cc) is taken in a disposable crimp-top vial evacuated to an appropriate vacuum level. Tests performed on these vials indicated that this vacuum level can be maintained for about 20 days. As the fluid is admitted into the sealed EDOSS vial, dissolved gases rapidly evolve from the fluid until equilibrium is achieved between the gases in the liquid and headspace. The evolved gases remain confined in the glass vial until analysis is completed. Gas analysis is carried out in the same vial, which now becomes the extraction vessel. As a result, this method provides a simple DGA procedure, with no subsequent liquid handling during gas extraction and analysis. The theory behind this method is identical to that of the EPOSS method, with the additional advantage of being able to use inexpensive and disposable vials as well as low cost shipping.

Theory of Headspace Analysis

The concentration of gases in the original sample can be calculated from a mass balance as proposed by Loffe and Vitenberg[1] and Markelov and Guzowski[12] The mass balance equation for a gaseous component *i* in the fluid phase is given by:

$$C_L^o V_L = C_L V_L + C_G V_G \qquad \text{(eq. 5-1)}$$

where C^o_L is the gas concentration of *i* in fluid; V_L , the volume of fluid introduced in the sampling vial; C_L, the equilibrium concentration of *i* in the liquid phase; V_G, the headspace volume and C_G , the equilibrium concentration of *i* in the gas phase. By substituting in eq. 5-1 the value of C_L for $S_i p_i$ (Henry's law), where S_i is the solubility and p_i the partial pressure of component *i*,, and C_G for p_i/RT, (ideal gas law), this equation is reduced to:

$$C_L^o = \frac{p_i}{RT}\left[\frac{V_G}{V_L} + S_i RT\right] \qquad \text{(eq. 5-2)}$$

The value of p_i is obtained from the mole fraction and the total gas pressure in the vial, according to Dalton's law ($p_i = P_T x_i$). The mole fraction of *i* (x_i) in the headspace is

measured with a gas chromatograph (GC) and the total pressure (P_T) is determined for each vial. The equilibrium temperature T corresponds to the temperature of the oven in the headspace analyzer. Each vial is weighed before shipment and weighed after it returns, thus, V_L can be calculated from the weight and density of the fluid. The internal volume of the vials is nearly constant for all vials from the same batch. As an example, the volume measured for 20 vials from one batch was found to average 21.33 +/- 0.10 cc, amounting to 0.5% variation. The volume of the headspace V_G can be calculated by the difference ($V_G = V_{vial} - V_L$).

The solubility (S_i) values for all gases in fluids of interest can be determined by rewriting eq. 5-2 as an expression of $1/p_i$ in terms of (V_{vial}/V_L), as follows:

$$\frac{1}{p_i} = \frac{1}{RTC_L^o}\left[\frac{C_{vial}}{V_L}\right] + \frac{1}{C_L^o}\left[S_i - \frac{1}{RT}\right] \qquad \text{(eq. 5-3)}$$

This equation represents a straight line of slope $m = 1/[RTC^o_L]$ and intercept $n = 1/C^o_L[S_i\text{-}1/RT]$. Data to solve eq. 5-3 was obtained by filling vials with different volume of a solution containing all gases of interest. The actual gas concentration of this solution is not required for solubility determinations since the GC detector response factors are determined with certified gas blends. From the partial pressure for each component in the vials, a linear regression of $1/p_i$ against V_{vial}/V_L is used to determine the slope (m) and intercept (n). The solubility for each component is thus calculated from:

$$S_i = \frac{1}{mRT}\left[n + \frac{1}{mRT}\right] \qquad \text{(eq. 5-4)}$$

This approach is limited to gases with solubilities larger than 1/RT. Fortunately, this holds true for most dissolved gases, with the exception of hydrogen.

Accuracy and Precision

The reproducibility of the EDOSS method was tested at a variable sample volume and constant sample volume. The results for the first case are shown in Table 5-1.

Table 5-1
Reproducibility of EDOSS Method with Variable Sample Volume

Volume (cc)/ Gas	2.3	4.5	6.0	7.6	8.0	9.9	Avg	Std Devtn.	CV%
Hydrogen	0	94	28	28	27	27	41	26	65
C. Monoxide	271	303	298	308	309	322	302	16	5
C. Dioxide	4,280	5,270	5,340	5,630	5,830	6,090	5,630	308	5
Nitrogen	70,700	77,300	73,200	72,400	72,600	73,100	73,200	2,000	3
Oxygen	179	78	287	152	368	1,023	213	103	48
Methane	52	57	53	56	58	58	56	2	4
Ethane	49	52	50	48	48	48	49	2	3
Ethylene	100	110	102	101	100	99	102	4	3
Acetylene	0	0	1.5	1.2	2.1	1.3	1.5	.3	23
Propane	89	102	93	95	96	97	95	4	4
Propylene	109	133	127	133	123	128	126	8	7
Isobutane	30	31	33	25	27	29	29	3	9
n-Butane	46	76	45	40	47	45	50	12	24
Isobutylene	199	188	180	171	151	148	173	19	11

This table shows a coefficient of variation below 11% for most gases independent of the sample volume taken in the vial. However, for gases present at very low concentrations or close to their detection limit (i.e. hydrogen) a volume larger than 4.5 cc must be utilized in order to improve the reproducibility.

The accuracy of the EDOSS method was established by comparing results with the EPOSS method for the same fluid samples. The accuracy of the EPOSS had previously been established through analysis of gravimetrically prepared fluid-gas solutions[4]. Table 5-2 shows the result of EPOSS accuracy determination with gravimetric solutions. The third column shows the error for a single sample, while the forth column shows the average for 5 samples. The error expressed as the percent of standard deviation over the average indicates an error range between -1.7% to -12.1% with an average of -6.5%.

Table 5-2
Accuracy Determination for EPOSS/DGA

Gas (ppm/v)	Actual	EPOSS	% Error[1]	%Error[2]
Methane	89	80	-10.5	-7.1
Ethane	119	106	-10.8	-8.5
Ethylene	139	128	-7.4	-12.1
Acetylene	57	50	-11.8	-8.0
Isobutylene	25	22	-13.2	3.4
Hydrogen	6,513	6,468	-0.7	-1.7
C. Monoxide	23	21	-8.0	-4.7

[1] Single test

[2] Average for 5 tests

Table 5-3
Accuracy and Reproducibility to the EDOSS Method

Gas (ppm)	#1	#2	#3	#4	#5	#6	#7	Avg EDOSS	%CV EDOSS	Avg EPOSS	%Diff
Hydrogen	128	137	136	143	138	144	148	139	4.2	122	14
Nitrogen	43,100	41,400	41,300	42,800	44,700	42,160	44,600	42,900	3.0	36,980	16
C. Monoxide	38	37	39	39	40	40	42	39	3.8	32	21
C. Dioxide	173	172	172	177	182	181	180	176	2.1	141	25
Methane	109	102	105	107	106	107	108	106	1.8	106	0
Ethane	162	154	157	161	158	159	160	159	1.5	152	5
Ethylene	192	183	186	191	188	190	193	189	1.6	167	13
Acetylene	66	63	64	65	64	66	66	65	1.6	59	10
Isobutylene	31	30	30	31	31	31	30	31	1.9	25	24

In Table 5-3, the DGA results for seven EDOSS and seven EPOSS analyses of a same fluid sample taken from a common source. The average and coefficient of variation for

the EDOSS results are given respectively in columns 9 and 10, while the average for the EPOSS results are given in column 11. The reproducibility of the EDOSS procedure was observed to vary from 1.6 to 4.2%, depending on the nature of the gas. This is in line with the previous results shown in Table 5.1 for sample volumes over 4.5 cc. Considering that the accuracy of the EPOSS procedure is already known. The accuracy of the EDOSS procedure can be estimated by comparing the average results from columns 9 and 11 in Table 5-3.

The accuracy of EDOSS respect to EPOSS varies from 0 to 25% with an average for the 10 gases considered of about 14%. In light of the low gas concentration range of the sample utilized in this determination and low sensitivity for carbon oxides, the accuracy of the EDOSS technique can be considered to be more than adequate.

6

CONCLUSIONS

Several mechanical components were designed and fabricated to develop a procedure based on an inexpensive disposable vial in which both sampling and analysis operations can be performed. This technique proved successful both in the laboratory and field conditions and is applicable to a variety of fluid-filled equipment. The following conclusions are made:

- a viable alternative to EPOSS, referred to as EDOSS, has been developed and successfully tested under field conditions
- EDOSS offers significant cost and handling advantages
- several components were devised and successfully tested to allow direct sampling of the fluid into disposable vials
- a micro pressurization system was assembled to facilitate the sampling of high viscosity fluids used in extruded cable terminations and low pressure SCLF cables
- an automated headspace analyzer was modified for the analysis of the dissolved gas with two gas chromatographs

7

REFERENCES

[1] Singh, N., Morel, O. E., Butucel, B. A., and Rochon, M. in "Development of an Oil Deterioration Test Method to Monitor the Condition of High-Pressure Fluid-Filled Paper Cables" *EPRI Final Report* EL-7488-L, November (1991)

[2] Singh, N., Morel, O. E. and Multani, S. K., in "Underground cable Gas-in-Oil Analysis", *ESEERCO Final Report* Project EP-86-43, May (1994)

[3] Singh, N., Morel, O. E. and Singh, S. K., "The Condition Monitoring of Fluid-Filled Taped Cables Employed in Underground Transmission Through Dissolved Gas Analysis", *IEEE Transaction on Power Delivery*, Vol. 10, No. 1, January (1995)

[4] Singh, N., Morel, O. E. and Singh, S. K., "A Novel Method to Monitor the Condition of Fluid-Filled Taped Cables Employed in Underground Transmission Through Dissolved Gas Analysis", *EEIC* Conference, Illinois, September (1995)

[5] Singh, N., Morel, O. E. and Singh, S. K. and Rodenbaugh, T. J., "Predicteive Maintenance of Fluid-Filled Taped Cables Through a Novel Dissolved gas Analysis Method: U.S. Field Experience", *CIGRE* Session 15/21/33-16 (1996)

[6] "Accurate Gas Analysis Reveals Damaged Cable Section", EPRI *Innovators*, RP 7895, IN-100114, October (1992)

[7] "Dissolved Gas Analysis Ensures Continued Operation of 115 kV High Pressure Fluid-Filled Cable System", EPRI *Innovators,* RP 7910, IN-101579, August (1993)

[8] "Dissolved Gas Ana;ysis for Underground Cables Saves PG&E from Expensive Power Outage", EPRI *Innovators*, RP 7910-01, IN-103491, September (1994)

[9] Kesting, R. E. and Fritzsche, A. K. in "Polymeric Gas Separation Membranes", John Wiley & Sons Inc., pp. 27 (1993)

[10] Morton, M. I. in "Rubber Technology", Van Nostrand Reinhold, pp. 317 (1994)

[11] Ioffe, B. V. and Vitenberg, A. G. in "Head-Space Analysis and Related Methods in Gas Chromatography", John Wiley & Sons (1982)

[12]Markelov, M. and Guzowski, Jr. J. P. "Matrix Independent Headspace Gas Chromotographic Analyisis", *Analytica Chimica Acta*, 276, 235-245 (1993)