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MEASUREMENT OF DENSITY AND EXPANSION COEFFICIENT OF LIGHT ARABIAN VACUUM BOTTOMS AT HIGH TEMPERATURES AND PRESSURES

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MEASUREMENT OF DENSITY AND EXPANSION COEFFICIENT OF LIGHT ARABIAN VACUUM BOTTOMS AT HIGH TEMPERATURES AND PRESSURES

by

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ABSTRACT

Expandable vessels were designed to measure the density and thermal expansion coefficients of liquid at elevated temperatures and pressures by the gamma-ray attenuation method. Light Arabian vacuum bottoms was tested from 70°C to 300°C at 13.8 MPa. Results agree well with literature data.

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MESURE DE LA DENSITÉ ET DU COEFFICIENT D'EXPANSION DES RÉSIDUS DE DISTILLATION SOUS VIDE DU PÉTROLE D'ARABIE LÉGER À DES TEMPÉRATURES ET DES PRESSIONS ÉLEVÉES

par

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RÉSUMÉ

Des récipients expansibles ont été conçus pour mesurer la densité et le coefficient d'expansion de liquides à des températures et des pressions élevées par la méthode d'atténuation gamma. Des essais ont été effectués sur des résidus de distillation du pétrole d'Arabie léger, de 70 °C à 300 °C, à 13,8 MPa. Les résultats concordent bien avec la documentation.

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INTRODUCTION

The liquid density and thermal expansion coefficient i.e., volume expansivity, of liquids are difficult to measure at high temperatures and pressures because systems under such conditions cannot be studied conventionally. These parameters are important for the petroleum industry when units are operating at elevated temperatures and pressures. A non-intrusive method to determine the density and alternatively the volume expansivity is by gamma-ray densitometry. An apparatus was designed to test the feasibility of the method and was built and operated by AECL under contract to EMR. The results of these studies are analyzed in this note.

The gamma-ray attenuation of light Arabian vacuum bottoms (LAVB) was measured by a narrow beam gamma ray using a Cs-137 source at 0.662 MeV in conjunction with a NaI(Tl) scintillator at temperatures from 100°C to 300°C at 13.8 MPa. With these data, the density as a function of temperature was determined. This function is observed to be linear in the range of temperatures studied and its slope is linearly related to the volumetric thermal expansion coefficient.

PRINCIPLE

At isobaric conditions, the attenuation of gamma rays for an empty and liquid filled vessel as a function of temperature can be approximated by linear relations:

$$N_o = A + B\ T \qquad \text{Eq 1}$$

$$N = C + D\ T \qquad \text{Eq 2}$$

where

A, B, C, D = constants

N_o = count rate for the empty vessel

N = count rate for the vessel filled with liquid

Since the attenuation of gamma rays follows Beer's law (1,2):

$$N = N_o \exp[-\mu X] \qquad \text{Eq 3}$$

where

X = the thickness of liquid being scanned
μ = the attenuation of liquid at temperature T (cm^{-1})

The attenuation coefficient can be expressed by (1):

$$\mu = K \rho (1 + w_h) \qquad \text{Eq 4}$$

where

K = a constant for a given gamma ray energy
ρ = the liquid density at temperature T
$\sim$ 1.023 g/cm^3 at 15^oC for LAVB (based on specific gravity)
w_h = the hydrogen weight fraction of the liquid

Equation 4 is a result of the fact that ratios of atomic weight to atomic number considered here are 2 for all elements except hydrogen, for which the ratio is 1.

The above equations give:

$$\ln[N/N_o] = - K \rho (1 + w_h) X \qquad \text{Eq 5}$$

Assuming there was no chemical reaction, w_h becomes a constant. Equation 5 leads to:

$$\rho = -\ln[N/N_o] / [K (1 + w_h) X]$$

$$= - \ln[N/N_o] / Q \qquad \text{Eq 6}$$

where the definition of Q is obvious. Using the known value of X, w_h and a predetermined density at any temperature, the value of Q can be determined.

The density as a function of temperature can also be approximated by the Taylor expansion with respect to properties at a reference temperature T_o as follows:

$$\rho = \rho_o + E\,(T - T_o) \qquad \text{Eq 7}$$

where

$$E = d\rho/dT \qquad \text{Eq 8}$$

subscript o: a reference condition

E relates to the well known thermodynamic parameter volume expansivity (3) or coefficient of thermal expansion (4), β, according to (3):

$$E = d\rho/dT = d(m/V)/dT = -(m/V^2)\,dV/dT$$

$$= -(m/V)\beta = -\rho\beta \qquad \text{Eq 9}$$

Combining Eq. 1, 2, 6 and 8, the following equation is obtained:

$$E = (BC - AD) / \{Q\,[AC + (AD + BC)T + BDT^2]\} \qquad \text{Eq 10}$$

Because usually $AC \gg (AD + BC)T + BDT^2$ (see results given below), Eq. 10 can be approximated as

$$E(T) = (BC - AD) / (QAC) \qquad \text{Eq 10A}$$

Equations 9 and 10 (or 10A) establish the relationship between the thermodynamic parameter volume expansivity and parameters measured by the gamma-ray attenuation method.

Frequently, there are possible systematic errors inherent in gamma ray attenuation measurements when a thick walled small vessel is used. For instance, there could be a slight misalignment of the gamma ray relative to the vessels between measurements on an empty and a filled vessel. In this case, it was observed either or both of the measured count rates in Eq. 1 or 2 could deviate by a nearly constant factor. This means that the observed N'_o and N' can be related to N_o and N for the ideal case by:

$$N' / N'_o = SN / N_o \qquad \text{Eq 11}$$

where

$$N'_o = A' + B'T \qquad \text{Eq 1A}$$
$$N' = C' + D'T \qquad \text{Eq 2A}$$

S = deviation factor (normally ~1)
Primes indicate measured values.

Equation 11 implies that the measured coefficients in Eq. 1A or 2A are related to Eq. 1 or 2 by

$$(A',B',C',D') = (A/S,B/S,C,D),$$
$$(A',B',C',D') = (A,B,SC,SD)$$
or $$(A',B',C',D') = (S_1A,S_1B,S_2C,S_2D) \text{ with } S = S_2/S_1.$$

Following these definitions, the density as a function of temperature can then be expressed by:

$$\rho = -\ln[N'(T) / N'_o(T)] / Q'$$
$$= -\ln[(C' + D'T)/(A' + B'T)] /Q'$$
$$= -\ln[S(C + DT)/(A + BT)] / Q' \qquad \text{Eq 12}$$

This gives,

$$E = d\rho/dT \sim S(BC - AD) / (Q'SAC)$$
$$= (B'C' - A'D') / (Q'A'C') \qquad \text{Eq. 13}$$

Equation 13 shows that if a density is known at any temperature, the expansion coefficient can be determined by the gamma ray attenuation method without precise alignment between empty and full vessel gamma beam positions.

EXPERIMENTAL AND RESULTS

The main consideration in the design of the apparatus was the need for a way to heat the liquid up at a high constant pressure (isobaric) without allowing the external gas to dissolve into the liquid. This was accomplished by using a sealed stainless steel container of 3.68 cm ID welded to a bellows (Part B of Fig. 1). The container was suspended within a pressure vessel (Part A of Fig. 1). The vessel was mounted on a height adjustable jack allowing the measurements to be made at various vertical positions, while the gamma densitometer could be adjusted horizontally. The vessel was connected to a high pressure tank of nitrogen or hydrogen. In addition, the pressure vessel was fitted with two flat plate electric heaters capable of heating the vessel to well over 300°C.

To find coefficients A', B', C' and D' in Eq. 1A and 2A for LAVB, the count rate of the empty container was first measured at temperatures from 100°C to 360°C. Each count rate was measured over a span of 70 seconds. The container was then cooled and filled with the liquid and the vessel was pressurized to 13.8 MPa. The count rates were then measured at various temperatures ranging from 70°C to 300°C. Gas was released as the temperature increased to ensure that the pressure remained at 13.8 MPa. Results are listed in Tables 1 and 2 which are plotted in Fig. 2 and 3, respectively.

By linear regression, constants in Eq. 1A and 2A are found to be:

$A' = 22864$ (counts/s); $B' = 0.583$ (counts/s °C)
$C' = 15788$ (counts/s); $D' = 3.655$ (counts/s °C)

Using the known value of $X = 3.68$ cm, $w_h = 0.1$ and the predetermined density of 1.023 g/cm^3 at 15°C, the value of Q' as determined by using Eq. 12 is 0.359 cm^3/g. By substituting A', B', C', D' and Q' into Eq. 13, we find $E = -5.74(10^{-4})$ g/cm^3. Therefore, from Eq. 7, the density for the light Arabian vacuum bottoms can be expressed by:

$$\rho = 1.023 - 5.74(10^{-4})(T - 15) \quad [g/cm^3, T \text{ in } ^oC] \qquad \text{Eq 14}$$

Densities can also be calculated from the following equation derived from Eq. 12:

$$\rho = -\ln[(15788+3.655T)/(22864+0.5834T)] / 0.359 \qquad \text{Eq 15}$$

Equation 15 was used to calculate densities of the liquid for some selected temperatures. Results are plotted in Fig. 4 which shows a good linear relation. The slope gives $E = -5.53(10^{-4})$ g/cm^3 ^{o}C which is very close to $-5.74(10^{-4})$ determined by Eq. 14. Furthermore, these values agree well with the literature value of $E = -6.0(10^{-4})$ g/cm^3 ^{o}C obtained from the well known correlation of density versus temperature for petroleum fractions with a specific gravity of 1.00 at 15^{o}C (5).

As a check, the density measured at 300^{o}C was measured and found to be 0.88 g/cm^3 under a hydrogen atmosphere at the same pressure by a different method using a CANMET hydrocracking pilot plant and was found to compare well with the value 0.86 and 0.87 g/cm^3 calculated, respectively, by Eq. 14 and 15.

It is noted in these feasibility tests that the value of Q' obtained in Eq. 13, 0.359 cm^3/g differs significantly from the theoretical value 0.30 cm^3/g for Q in Eq. 6 by using K = 0.073 calculated from the attenuation coefficient diagrams given in the literature (1). This discrepancy can be attributed to systematic errors encountered in the experiment such as imperfect alignment for the gamma ray through the grooved channel on the pressure vessel as shown in Fig. 1 and parameters assumed for calculations. Despite the difference between Q and Q', the accuracy of results is remarkable indicating that the technique is positively proven both theoretically and empirically. The design of improved durable vessels for industrial applications is worth pursuing.

In principle, the thermal expansion coefficient can also be calculated from the expansion of the vessel measured by the vertical scan using the gamma ray. However, no consistent results were obtained. This was possibly because of a small amount of gas being released at an elevated temperature causing a large uncertainty.

Knowing the density as a function of temperature, i.e., Eq. 14 or Eq. 15 and the corresponding E value, the expansion coefficient, i.e., volume expansivity, can be easily calculated from Eq. 9. Results for some selected temperatures are listed in Table 3. Those values agree very well indicating the approximated Eq. 13 is adequate.

CONCLUSIONS

Expandable vessels were designed and successfully tested for the measurement of density as a function temperature and thermal expansion of LAVB at 13.9 MPa using the gamma-ray attenuation technique. The results are very satisfactory even though experiments were conducted as feasibility studies.

The density change with respect to temperature was found to equal -5.74 g/cm^3 ^oC. It is believed that a more accurate value could be obtained if the system were better calibrated.

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Table 1 - Count rate of the empty vessel as a function of temperature

Temp (^oC)	N_o (counts/s)
108	22930
154	22940
255	23032
301	23044
356	23060

Table 2 - Count rate as function of temperature when the vessel filled with LAVB

Temp (^oC)	N (counts/s)
70	16021
100	16171
150	16320
200	16555
240	16653
275	16831
300	16841

Table 3 - Comparison of densities and expansion coefficients obtained form approximated and original equations

	Approximate method (Eq. 14)		Non-approximate method (Eq. 15)	
Temp oC	Density g/cm^3	Exp coeff $^oC^{-1}$	Density g/cm^3	Exp coeff $^oC^{-1}$
50	1.003	$5.72(10^{-4})$	1.003	$5.51(10^{-4})$
100	0.974	$5.91(10^{-4})$	0.975	$5.67(10^{-4})$
150	0.946	$6.07(10^{-4})$	0.947	$5.84(10^{-4})$
200	0.917	$6.26(10^{-4})$	0.920	$6.01(10^{-4})$
250	0.888	$6.46(10^{-4})$	0.893	$6.20(10^{-4})$
300	0.860	$6.68(10^{-4})$	0.866	$6.39(10^{-4})$

Fig. 1 - Vessels for liquid density measurements at elevated temperatures and pressures: (A) Outer vessel for temperature and pressure control and (B) Sample vessel with expandable bellow

Fig. 2

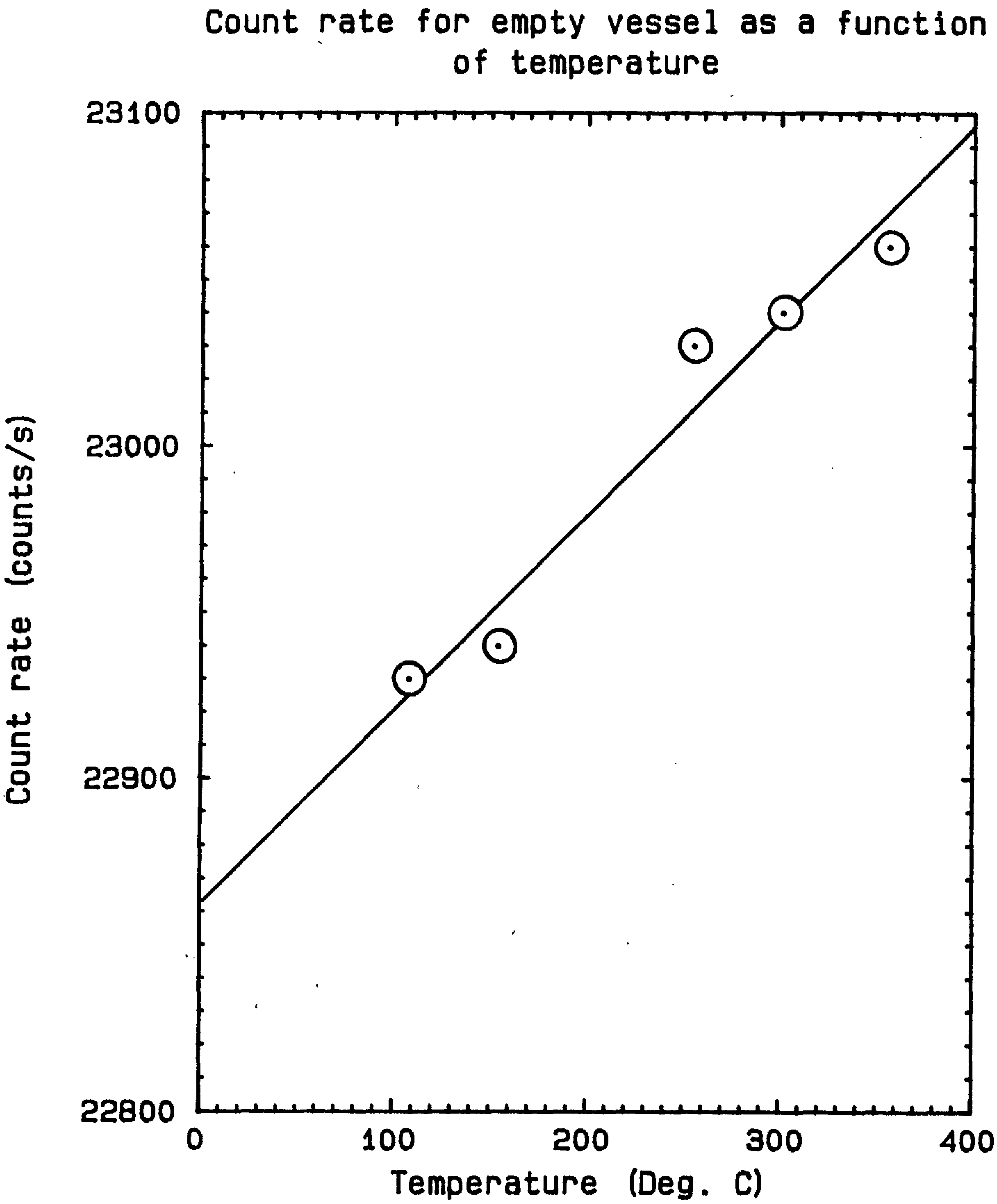
Count rate for empty vessel as a function of temperature
23100
23000
22900
22800
Count rate (counts/s)
0
100
200
300
400
Temperature (Deg. C)

Fig. 3

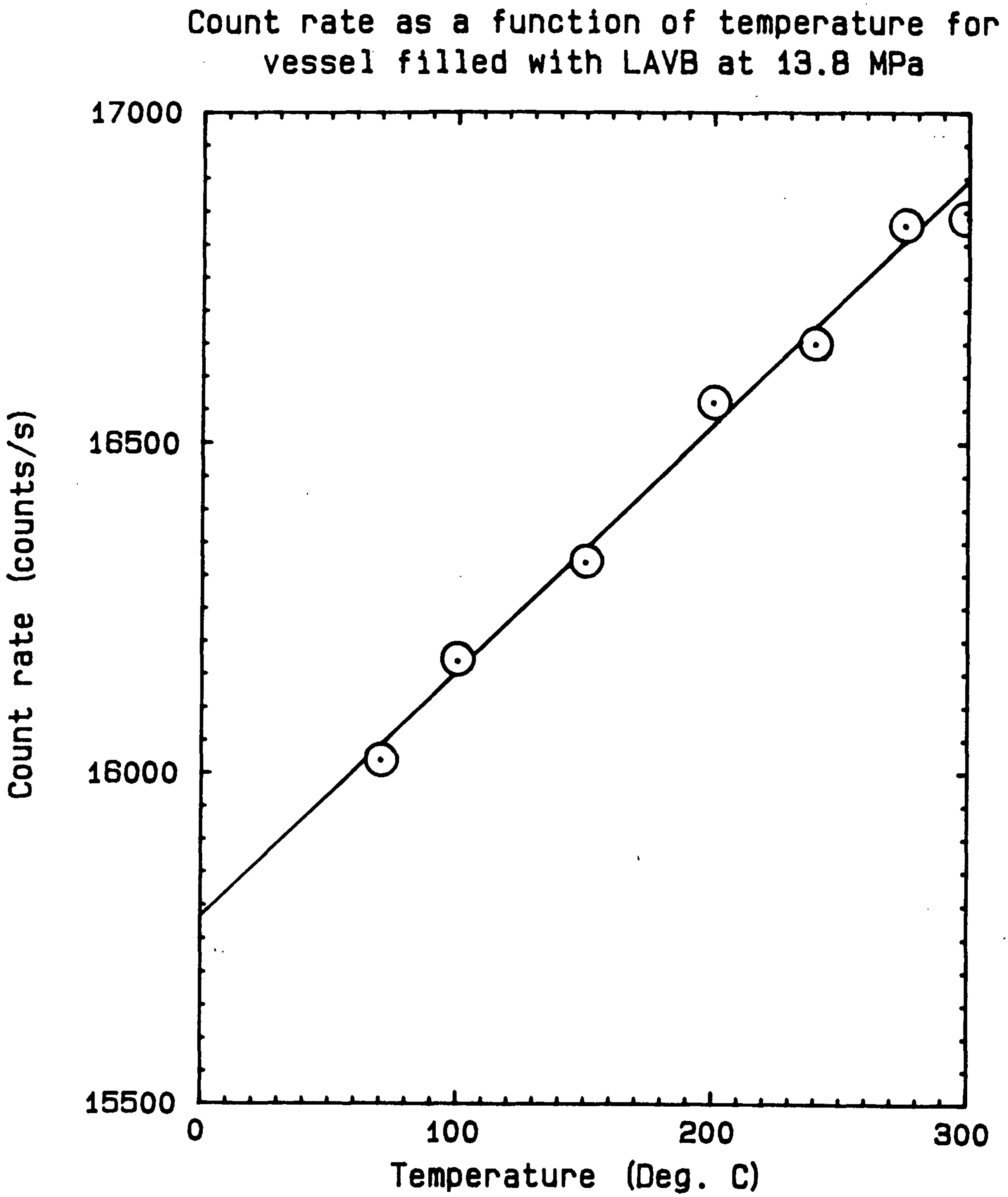
Count rate as a function of temperature for
vessel filled with LAVB at 13.8 MPa
17000
16500
16000
15500
Count rate (counts/s)
0
100
200
300
Temperature (Deg. C)

Fig. 4
Density of LAVB as a function of time