CHAPTER 6

AREAS OF PROMISE FOR THE DEVELOPMENT OF FUTURE PRIMARY FREQUENCY STANDARDS

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Contents

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"Brief words, when actions wait are well: The prompters hand is on the bell—Behind the curtain's mystic fold The glowing future lies unrolled."

Francis Bret Harte

This paper discusses possibilities which may lead to the development of future primary frequency standards of superior accuracy capability. Aspects of cost and field-usage are totally neglected. A review is given of the various methods and techniques which are currently employed in quantum electronic frequency standards or which have a potential usefulness. Various effects which influence the output frequency of a primary standard are associated with these methods. They are discussed in detail, and expectation values for the related uncertainties are given. For selected particles certain methods of interrogation, confinement, and particle preparation can be combined such as to minimize the net uncertainty due to all applicable effects. Different technical solutions are the result. A review of existing and proposed devices is given, including quantitative data on the stability and accuracy capability. Aspects of the most promising devices are discussed, and it is concluded that accuracy capabilities of 10^{-14} should be within reach of today's research and development.

Key words: Accuracy (frequency standards); figure of merit; frequency stability; future primary frequency standard; gas cells; ion storage; masers; particle confinement; particle interrogation; particle preparation; primary frequency; quantum electronic frequency standards; storage beam.

6.1. INTRODUCTION

A primary frequency standard is based ultimately on some fundamental property of nature. The actual realization of an output frequency involves several steps of physical and technical processing. Each of these steps may cause a more or less pronounced shift of the output frequency of the standard. The magnitude of each shift must be evaluated theoretically and experimentally. The resulting corrections are called the biases; however, they are never known exactly but have associated with them uncertainties. The magnitudes of these uncertainties depend on the degree of theoretical understanding, on experimental parameters, and on their measurability. The combined uncertainty of all biases is referred to as the accuracy capability of the frequency standard.

At present the standard with the highest accuracy capability is the cesium atomic beam tube. This fact is reflected in the agreement at the 13th General Conference on Weights and Measures (1967) to define the second as the duration of 9192 631 770 cycles of the unperturbed radiation of the Cs^{133} hyperfine transition $(F = 4, \ m_F = 0) \longleftrightarrow (F = 3, m_F = 0)$. The cesium beam tube, although it still can be improved, is already at a very advanced stage of technical development. An accuracy capability of the order of parts in 10^{13} is now a reality which is achieved in several laboratories around the world [1—5]. However, a natural demand exists for an even more accurate definition, and frequency standards of extreme precision will be needed in various technical applications. New aspects of scientific, technical, and metrological importance have evolved because of recent successes in multiplication of frequencies into the infrared region of the electromagnetic spectrum [6—10]. A substitution of conventional length (wavelength) measurements by much more precise and accurate frequency measurements will soon be possible and may ultimately lead to a unified (frequency) standard for frequency, time and length with the speed of light being a defined constant. We may look even further ahead to the possibility that other basic physical quantities, e.g., the volt via the Josephson effect, will be based on the same (frequency) standard. This illustrates the far reaching importance which we have to attribute to the development of primary frequency standards.

In the following we will compare and discuss possibilities in methods and techniques which are at our disposal for pushing the fractional frequency accuracy capability beyond 10^{-13}. This will be done in a way which differs somewhat from the usual approach of comparing different existing devices [11]. Instead we will compare the methods and techniques used in quantum electronic frequency standards, and we will try to synthesize from these an optimized device. As the criterion for excellence in this comparison it appears best to choose accuracy capability as the prime topic in our discussions. The influences affecting the frequency of a quantum electronic frequency standard can be grouped into three classes: (1) effects associated with the interrogation of the atoms or molecules, (2) effects related to the method of confining the particles, and finally (3) effects associated with the particles themselves and with the way in which they are treated for an effective interrogation by electromagnetic fields.

We will discuss these three groups successively in more detail. Since we are aiming for accuracies of better than the present state-of-the-art (parts in 10^{13}) we will discard as unimportant only those effects which lead to fractional uncertainties of less than 10^{-14}. At this point it should be emphasized that the following discussion is based on our present state of knowledge. There might well be other methods and techniques which could be used, and there might be additional sources of uncertainty of which we are not yet aware. We also are not going to discuss basic physical and engineering details of the various techniques and devices. They may be found in the referenced literature. In particular, Refs. [11—15] will give an introduction to the problem area in historic perspective.

6.2. EFFECTS ON FREQUENCY: PARTICLE INTERROGATION

In a quantum electronic frequency standard we are

not only concerned with the actual quantum transition of the particles (clock transition) involved but also with the production of an output signal. In general two different tasks are to be accomplished: (a) the generation of a signal which is to be compared with the actual "clock" transition, and (b) the generation of a useful standard frequency output. It is obvious that at least one oscillator—in general, more than one—is necessary for these tasks. These slave oscillators may be quartz crystals, klystrons, lasers, or any other suitable devices. They must be locked in frequency or in phase to the "clock" transition. This can be accomplished by four distinctly different methods: The active maser oscillator [16—19], whereby its output frequency is compared to a synthesized frequency derived from the slave oscillator; the absorption [20—22] or amplification [16] of an electromagnetic frequency by the atomic or molecular transition; the detection and counting of the number

Table 1. *Effects on frequency; Particle interrogation*

Methods	Effects
Active: Self-oscillation	Noise in:
Passive:	Detector
Absorption or amplification	Receiver
of radiation	Resonance structure
Particle detection	Multiplier and synthesizer
Frequency transformation	Quantum transition
	Slave oscillator fluctuations
	Spectrum asymmetry
	Cavity pulling
	Interrogating radiation

of particles having undergone a transition caused by a signal which is derived from the slave oscillator [1, 23, 24]; and finally the observation of transitions by their effect on other transitions of different frequencies to which the "clock" transition is coupled [25] (frequency transformation). In the first column of Table 1 the different interrogation methods are summarized.

The second column lists various effects which give rise to bias uncertainties and which are associated with one or more of the methods of interrogation.

The fractional frequency stability [26] of a quantum electronic frequency standard may conveniently be written as

$$\sigma_y \equiv \frac{K}{M} \frac{1}{\sqrt{\tau}} .\qquad(1)$$

The symbols in (1) have the following meaning: τ is the measurement interval; M is a basic figure of merit[1] given by

$$M \equiv \sqrt{n_s}\, T_r ,\qquad(2)$$

where $T_r \equiv$ relaxation time, and $n_s \equiv$ flux of signal particles. The constant K contains the device characteristics. As examples we have for particle detection [24, 26] (which includes detection of photons with $h\nu >> kT$)

$$K_{passive} \gtrsim \frac{1}{2\,\pi\nu} ,\qquad(3)$$

and for an active oscillator (with $h\nu << kT$) [16,26] we have

$$K_{active} \gtrsim \frac{1}{\sqrt{2}\,\pi\nu} \sqrt{\frac{kT}{h\nu}} .\qquad(4)$$

From these equations we see that the flux of signal atoms and the relaxation time which make up our basic figure of merit M are not the only important parameters in determining frequency stabili'y. The principle which is used in the interrogation of the particles is also important, and is reflected in the value of K. For example at $h\nu << kT$ a device (with the same M for each version) will have a better noise performance when passive particle detection is used as compared to using the mode of operation as an active quantum electronic oscillator [27]. This can be seen by comparing (3) and (4). Also, additive thermal noise at any reasonable particle or photon intensity is negligible, and excess noise contributions of particle or photon detectors are typically very low. Thus shot noise of the incoming particles is usually the only limitation. In contrast we almost always will encounter additional noise in an active (maser) oscillator because of performance limitations in its microwave receiver.

Another potential noise source is the frequency multiplier and synthesis chain connecting the slave oscillator to the "clock" transition. The current state-of-the-art is such that this noise contribution is negligible compared to the noise due to the slave oscillator [1, 28]. Noise can also be associated with the quantum transition itself, i.e., in the form of spontaneous emission. Such effects will become more serious at higher (optical) frequencies because the probability for spontaneous transitions increases as the cube of the transition frequency.

The short-term stability of the slave oscillator is of equal importance for all methods because its performance determines the stability of the whole standard at short averaging times [26]. The only remedy is the development of good slave oscillators.

Spectral asymmetry of the interrogating signal is of concern for all passive devices [29, 30]. It can be reduced to unimportance by adequate care in the electronics. Also the choice of a low frequency transition might be helpful. In active devices this problem is practically non-existent.

For many devices a resonance structure (cavity) is necessary to create the required strength and spatial distribution of the interrogating electromagnetic field. This leads to the possibility of cavity pulling which may be written as [16, 29]

$$\Delta\nu \equiv G\,\Delta\nu_c \qquad(5)$$

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[1] This M differs from traditional figures of merit found in the literature.

where $\Delta\nu_c$ and $\Delta\nu$ are the offsets of the cavity and the output frequencies respectively. For an active oscillator the parameter G is approximately the ratio of the widths of clock transition and cavity resonance [16], for passive methods (sufficiently far from self-oscillation) G is approximately the square of this ratio [29]. Thus an active oscillator is inherently more affected by cavity pulling than a passive device. Moreover a sharp cavity resonance, i.e., a larger G, is a prerequisite for an active oscillator [16] whereas a broad cavity resonance or—at least in principle—no resonance structure at all, i.e., $G = 0$, can be used with passive methods. Cavity pulling is therefore only of concern to active oscillators.

For laser oscillators we have $G \approx 1$ which rules out their use as frequency standards. The stability of the output frequency would be directly given by the mechanical stability of the optical resonator.

The last item in Table 1 is the effect caused by the interrogating signal itself. One example is the Bloch-Siegert frequency shift [30]. The fractional frequency shift is related to the power of the interrogating signal and can be expected to be negligible for all techniques under discussion if excessive power levels are avoided [30]. Another example is the recoil effect which may be a serious limitation if the photon energy of the interrogating radiation is large (infrared and optical frequencies). They are discussed in more detail later in this paper under Conclusions.

We summarize: A passive method is to be preferred over an active oscillator. In addition a passive method offers more flexibility and freedom for evaluating bias corrections and accuracy limitations, because a passive technique is not tied to meet an oscillation threshold condition. A low frequency (microwave) transition eliminates some of the problems; however, higher frequencies (infrared) may be used if technical problems associated with the multiplication process[2] can be adequately solved. At high frequencies (optical) effects associated with photons of higher energy (recoil) could represent a serious limitation.

6.3. EFFECTS ON FREQUENCY: PARTICLE CONFINEMENT

A quantum electronic frequency standard is based ideally on the quantum transition of a particle (atom or molecule) which is in an unperturbed state and is interrogated for an indefinite period of time.

In principle this may be achieved by confining an ensemble of particles to that region of space which is filled with the interrogating radiation and to accomplish this confinement in such a manner as to minimize the perturbation of the individual particles. In reality it appears possible to realize the ideal of a free particle to a very good approximation; however, it is at the expense of interrogation time, and vice versa.

Various methods of confinement are at our disposal. We may use a beam of free particles travelling in vacuum through the region of space where interrogation takes place [22, 23]. We may store the particles in the region of interrogation at low particle densities by using storage vessels. The storage vessel has to be coated [31, 32] or filled with a buffer gas [17, 33] in order to reduce the interaction between the particles and the wall of the storage vessel and among particles themselves. Or we can do away with physical walls and use electric or magnetic fields for confinement [34]. Finally, we may just take a gas at a fairly high pressure and observe absorption [20, 21] of the interrogating radiation. A summary of these methods is given in the first column of Table 2.

Various effects (listed in the second column of Table 2) which lead to bias uncertainties are introduced by the confinement of particles.

Several effects are associated with the line-Q which is proportional to the product of confinement time and transition frequency. They include short term stability, cavity pulling, and the performance of the servo electronics. A high line-Q is desirable but not essential because means can be employed to counter the effects of a low line-Q, e.g., one could render cavity pulling totally unimportant, regardless of the line-Q, by avoiding a resonance structure (using a passive method). On the other hand a high line-Q can be obtained with relatively short confinement times by using transitions at high frequencies. For achieving a long duration of confinement, i.e., in excess of one second, storage methods offer the greatest potential, especially the coated vessel or the usage of confining fields (ion storage). Collisions between the particles which lead to spin exchange and shifts of the energy levels are an important source of uncertainty in techniques using comparatively high particle densities. Low density methods like the free beam, the storage in a coated bulb, or the usage of confining fields can be designed to render this effect unimportant. We also may arrange the interrogation mode in such a way as not to look at particles which have experienced a collision, e.g., as in saturated absorption [20]. Wall collisions will introduce uncertainties wherever physical walls are used as a means of confinement. Only the free beam and the

Table 2. *Effects on frequency: Particle confinement*

Methods	Effects
Traveling free beam	Line-Q
Storage in:	Particle-particle collisions
Coated vessel	Wall interaction
Buffer gas	1st order Doppler
Electric or magnetic fields	2nd order Doppler
Absorption cell	Cavity phase shift

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[2] We may assume that multiplication, in principle, is possible.

confinement by fields are not affected[3]. However, we may also use an absorption cell and restrict the region of interrogation to a small volume within the cell [20], e.g., by using a laser beam as the interrogating radiation, thus avoiding wall effects. The first order Doppler effect appears to be mainly a design and engineering problem and thus of no real consequence for this discussion. We may assume that a suitable approach in all of the discussed methods will eliminate first order Doppler frequency shifts and line broadening. This may be done by proper interrogation (e.g., saturated absorption [20]), by storage within dimensions less than one half of a wavelength of the interrogating radiation [18], or by a proper mechanical design as required in the case of a free beam traveling through a Ramsey cavity [23]. The second order Doppler shift is of a more fundamental nature. It can be regarded as the problem to know with adequate precision the speed or temperature of the particles. This is difficult in the case of the free beam and is a severe problem in the case of storage in electric or magnetic fields, whereas the use of physical containers allows an adequate knowledge of the temperature, when thermal equilibrium of the kinetic energy of the particle with the container walls can be established. Cavity phase shift offsets occur in the case of the free beam traveling through a cavity [1—5]. For all other methods it is of no concern.

We summarize: The choice of a high frequency transition is to be preferred because this leads to a reduction of the fractional importance of most effects; the Doppler shifts, of course, are excluded. Thus the (second order) Doppler limitation favors the storage in containers where thermal equilibrium exists between the kinetic energy of the particles and the walls of the storage vessel. At low (microwave) frequencies we cannot single out a specific method of confinement as being inherently superior to others.

6.4. EFFECTS ON FREQUENCY: PARTICLES AND PARTICLE PREPARATION

The particles which we choose are either atoms or molecules, and we may use any of the different types of electric or magnetic dipole transitions. In order to effect interrogation, the particles are generally prepared so that this can be done efficiently. Preparation usually means the creation of a population difference of the energy levels which differs from (is larger than) the thermal distribution.

Only at high frequencies, above one terahertz, does the preparation of particles lose its importance, because of the large population differences already present in thermal equilibrium. This allows efficient absorption of the interrogation signal without preparation. Possible methods of preparation are listed in the first column of Table 3.

Spatial state selection achieves the change in population difference by eliminating one or more energy states from a particle beam[4] [35]. This method is based on differences in the electrostatic or magnetic forces acting in inhomogeneous electric or magnetic fields on the electric or magnetic dipole moments which are associated with each energy state. Optical pumping can be used which causes changes in population difference when the pumping light acts on the energy levels selectively by proper use of polarization, filtering [36], etc. Electron collisions can be used to alter the population of the energy levels from the thermal equilibrium values. As examples, electron beams of well defined energy or a gas discharge can be employed. A change in population can also be accomplished by spin exchange collisions with atoms or molecules which have already been polarized by any of the other methods [34]. Chemical effects may be used such as a chemical reaction or a dissociation which lead to the formation of excited particles.

Again we find various effects associated with the different methods which give rise to bias uncertainties. They are listed in the second column of Table 3. The influence of external electric fields can be made unimportant if magnetic dipole transitions such as the hyperfine transitions in atoms are used [37]. Magnetic fields can be rendered unimportant when certain molecular transitions are taken [38]. Shielding will reduce the effects of both. Majorana transitions may occur if particles travel through regions of varying static field strength and thus are mainly of some importance for spatial state selection. Frequency uncertainties are introduced by transitions from neighboring states. This effect can be minimized by the choice of particles with a simple energy level structure and by carefully avoiding the stimulation of neighboring transitions.

Two classes of effects, listed in Table 3 as collisions and coupling of transitions, represent significant sources of frequency bias (and uncertainty) for all methods other than spatial state selection and absorption. Coupling of transitions occurs when the pumping radiation is present simultaneously with the interrogating radiation. Collisional effects will be encountered when collisions are used as a means of altering the population difference. The very method used for particle preparation is the source of a frequency bias (and uncertainty), and the more efficiently the preparation is made, the more restrictive is its effect on the performance as a primary frequency standard. In principle, we have a solution. In analogy to spatial state selection we may separate spatially the process of particle preparation from the particle interrogation. This can be done, for example, with two storage vessels connected by a diffusion channel or by using a traveling beam. An alternate solution is the

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[3] For the case of a magnetic dipole transition this is true when the particles (ions) are confined by electric fields.

[4] This method dates back to the famous Stern-Gerlach experiment.

separation in time of particle preparation and interrogation (pulsed preparation). However, we must

Table 3. *Effects on frequency; Particles and particle preparation*

Methods	Effects
Atoms	Electric fields
Molecules	Magnetic fields
No preparation (absorption)	Majorana transitions
Spatial state selection	Neighboring transitions
Optical pumping	Coupling of transitions
Electron collisions	Collisions
Spin exchange	
Chemical reaction	

realize that both solutions will encounter technical problems in their practical realization although they are fundamentally feasible.

We summarize: An atom or molecule should be used which has a simple energy level structure and properties which reduce the effects of external electric and/or magnetic fields. Obviously, the best choice for a particle preparation method is no preparation at all (simple absorption). However, we must then use transitions in at least the low terahertz range where the population difference in thermal equilibrium is sufficiently large for efficient interrogation. The optimum method of particle preparation at low (microwave) frequencies appears to be the spatial state selection.

6.5. EXISTING CONCEPTS FOR QUANTUM ELECTRONIC FREQUENCY STANDARDS

We will discuss only those quantum electronic frequency standards with a current or potential accuracy capability of better than one part in 10^{10}. Several devices have been developed, and some are even commercially available. They include the forerunner of all, the ammonia maser [16, 39], the rubidium gas cell [40], the cesium beam tube [1—5. 23], and the hydrogen maser [18, 19]. Two more devices have had a preliminary evaluation but are not nearly as mature as those previously mentioned: the thallium beam tube [41, 42] and the rubidium maser [17]. Several more concepts are being proposed or are in the early stages of experimentation. They include saturated absorption of laser radiation (methane [20], iodine [21], sulfurhexafluoride [43], etc.), simple absorption of laser radiation by a traveling beam (iodine [22]), other beam tubes (barium oxide [44]), ion storage (helium [34], mercury, etc.), and the storage beam tube (hydrogen [27]).

We will now look into the basic operating principle of each device and discuss briefly the chief limitation of each by comparing with Tables 1 to 3. It must again be emphasized that any effect imposing an accuracy limitation of worse than one part in 10^{14} will

count as a limitation. No attempt will be made at quoting quantitatively these limitations. For those devices which have been evaluated, the reader is referred to the published data in the referenced literature. For all other devices and concepts it seems futile to quote data which cannot adequately be supported. In order to form his own opinion the reader should consult the referenced literature. Finally it must be emphasized that the limitations quoted here
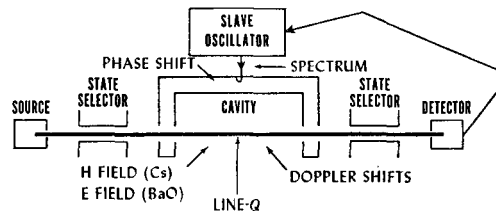

Fig. 1. Traveling beam tube

should not be regarded as final. They merely reflect the present state of our knowledge, and future work is likely to change them.

(a) Traveling Beam Tube (Fig. 1). The beam of particles originates at a suitable source or oven and travels through a first state selector which focuses only certain, desired energy states into the cavity region. Here the particles are interrogated by a microwave signal. As a result the distribution of particles into the various energy states is altered when the particles leave the cavity region. This is analyzed by a second state selector which focuses particles in selected energy states on a detector thus generating the error signal for a slave oscillator. Limitations are the spectrum of the interrogating radiation (Table 1); the phase difference between the two sections of the Ramsey cavity, the second order Doppler shift due to the uncertainty in the mean square particle velocity, and the relatively low line-Q (Table 2); and in the case of cesium and barium oxide the effects of fields (Table 3).

(b) Absorption in a Beam (Fig. 2). The beam of particles originates in a source and travels freely through a vacuum chamber. A laser which serves as the slave oscillator radiates perpendicularly onto the particle beam. Changes in the intensity of the laser radiation due to absorption in the beam can be detected (in-line position in Fig. 2), or alternately the intensity of the fluorescence radiated by the traveling beam may be monitored (displaced position in Fig. 2). Limitations are the spectrum of the laser radiation and the radiation itself via photon effects (Table 1); and the first and second order Doppler effects (Table 2).

(c) Traveling Beam Maser (Fig. 3). The only example is the ammonia maser. A beam of molecules leaves the source, is state selected, and enters a cavity which is tuned to the transition frequency. Because of the short interaction time between the particles and

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the microwave field in the cavity a large particle flux is required to obtain self-oscillation. Also, the delivery
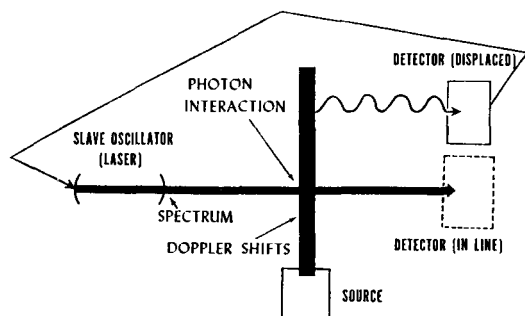

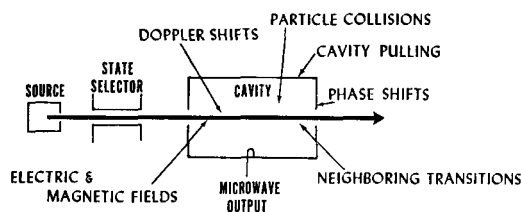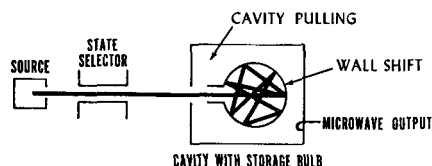Fig. 2. Absorption in a beam

Fig. 3. Traveling beam maser

Fig. 4. Storage beam maser

of the energy from the molecules to the cavity is in general not uniform and not symmetric along the length of the cavity. This together with the more complex level structure of ammonia leads to the following: Cavity pulling (Table 1); first and second Doppler shifts, particle collisions, and cavity phase shifts (Table 2); and electric fields, magnetic fields, and the influence of neighboring transitions (Table 3).

(d) Storage Beam Maser (Fig. 4). The only example is the hydrogen maser. A state selected atomic beam is generated in a fashion similar to the beam tubes. The atoms are stored in a coated bulb located within a cavity. The maser will oscillate provided certain conditions are met which relate to cavity- and line-Q, particle flux, and device geometry. Limitations are cavity pulling (Table 1); and wall interaction due to the storage principle (Table 2).

(e) Storage Beam Tube (Fig. 5). The hydrogen storage beam tube is a hybrid between the hydrogen storage beam maser and the traveling beam tube. The operation is analogous to beam tubes; however, the

hydrogen storage principle is adopted from the hydrogen maser. The direct flow of atoms from entrance to exit of the bulb must be prevented. A beam stop might be used, for example. The only serious limitation of this device is the wall shift (Table 2).

(f) Optically Pumped Gas Cell (Figs. 6 and 7). Examples are the rubidium maser (Fig. 6) and the rubidium gas cell (Fig. 7). Their basic concepts are
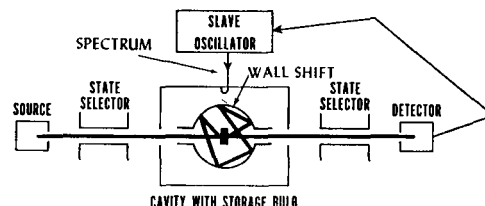

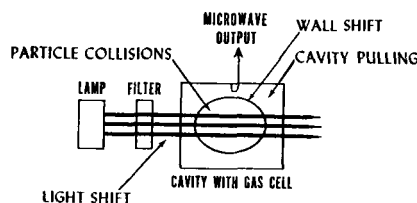Fig. 5. Storage beam tube

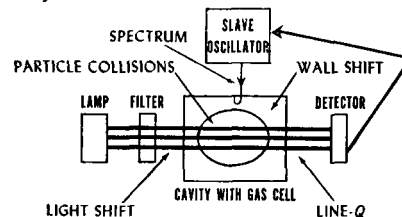Fig. 6. Optically pumped gas cell maser

Fig. 7. Optically pumped passive gas cell

quite similar. A filtered light beam optically pumps the rubidium which is stored, together with buffer gases, in a cell within a cavity. The maser will start oscillations under certain conditions. The passive gas cell obtains the error signal for a slave oscillator from a photocell which monitors the transmission of light through the gas cell. Thus a method which was called frequency transformation in Table 1 is used here, since the optical transmissivity is a function of the microwave signal applied to the cavity. Limitations are cavity pulling (maser only) and the spectrum of the interrogating radiation (passive device only) (Table 1); particle collisions, wall interaction, and a relatively low line-Q (Table 2); and the effects caused by the coupling of the clock transition to the optical pump transition which usually are called "light shifts" (Table 3).

(g) Saturated Absorption (Fig. 8). A gas cell is used which is irradiated by intense radiation from a laser which acts as the slave oscillator. Unique advantages of the saturation of an absorption are the significant reduction of the first order Doppler effect and the automatic exclusion from interrogation of most of the molecules which have suffered a collision. Known limitations are the spectrum of the laser radiation as well as photon effects of this radiation itself (Table 1); and particle collisions (Table 2).

(h) Ion Storage Principle (Fig. 9). Ions are confined by an inhomogeneous rf field, and can be stored for fairly long time periods. The confining field may be generated in a quadrupole trap consisting of a hyperbolic doughnutlike ring with hyperbolic caps on top
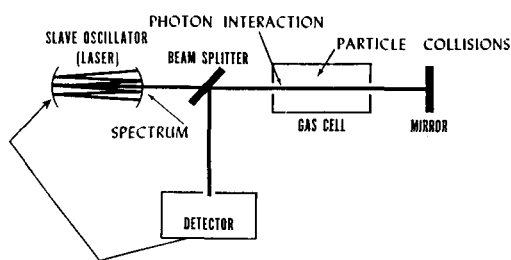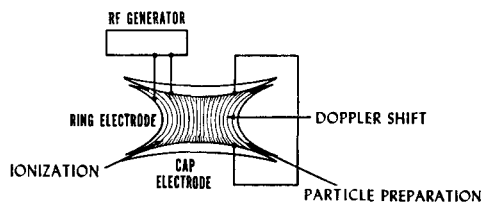

Fig. 8. Saturated absorption

Fig. 9. Ion storage principle

and bottom[5]. Limitations are imposed by the necessity to ionize and by the method of particle preparation, which, so far, is usually spin exchange with an injected polarized atomic beam. Comments on this aspect were

already made in Section 3. The most severe limitation is the second order Doppler effect (Table 2).

6.6. FREQUENCY STABILITY FOR ONE SECOND AVERAGING

In the previous discussion we did not include the aspects of random uncertainty. These aspects can be described quantitatively by (1) through (4). In Table 4, an attempt at this is made for the different existing concepts, whereby we choose the best understood actual system in each case, e.g., we use the actual (NBS-III)[1] and projected (NBS-5)[1] performances of cesium laboratory standards in the case of the beam tube concept.

The first column lists n_s, the signal particle flux or the number of interrogated particles per second; the second column gives the interrogation time T_r. In the third column the figure of merit M is calculated from (2). With the transition frequencies, which are listed in the fourth column, we can calculate from (1), (3), and (4) the fractional stability for 1 sec averaging time. It must be emphasized that the values given for n_s and T_r and therefore for σ are only approximate and sometimes only "educated guesses." However, they may serve to give an approximate feeling for the potential stability performance of each technique. We also must note that the measured stability usually will be worse than the calculated stability because of limitations in the associated electronics, i.e., receiver or detector, slave oscillator, etc. For example the best actual performance of the hydrogen maser is $\sigma(1s) \approx 8 \times 10^{-13}$ [45] (5×10^{-13} [46]) and of the methane saturated absorption is $\sigma(1s) \approx 2 \times 10^{-12}$ [20] (2×10^{-13} [47]).

6.7. ACCURACY CAPABILITY

At the beginning of section 4 we pointed out the difficulty in quoting quantitative values for the various error sources which make up the accuracy capability. Nevertheless it is of interest to quote those accuracy capabilities which have been determined for actual systems based on experiments. They are listed in the

Table 4. *Data on different concepts for primary frequency standards*

	n_s (s^{-1})	T_r (s)	M (s$^{1/2}$)	ν (Hz)	$\sigma_y \equiv \dfrac{K}{M}\dfrac{1}{\sqrt{\tau}}$ ($\tau = 1s$)	Accuracy capability	
						Present experimental performance	Projected
Traveling beam tube (Cs)	10^8	10^{-2}	10^2	9.2×10^9	2×10^{-13}	5×10^{-13} [1]	1×10^{-13}
Absorption in beam (I$_2$)	10^8	10^{-6}	10^{-2}	5.8×10^{14}	3×10^{-14}	—	better than 10^{-12}
Traveling beam maser (NH$_3$)	10^{13}	10^{-4}	3×10^2	2.4×10^{10}	5×10^{-13}	10^{-11} [48]	10^{-11}
Storage beam maser (H)	10^{12}	1	10^6	1.4×10^9	10^{-14}	2×10^{-12} [49]	better than 10^{-12}
Storage beam tube (H)	10^8	1	10^4	1.4×10^9	10^{-14}	—	better than 10^{-12}
Optically pumped gas cell (Rb)	10^{14}	10^{-2}	10^5	6.8×10^9	10^{-14}	10^{-10} [17]	10^{-10}
Saturated absorption (CH$_4$)	10^{10}	10^{-5}	1	8.8×10^{13}	2×10^{-15}	10^{-11} [20]	better than 10^{-12}
Ion storage (^{3}He$^+$)	10^5	10	3×10^3	8.7×10^9	10^{-14}	10^{-9} [34]	better than 10^{-12}

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[5] Several other trap configurations are possible.

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fifth column of Table 4. There are no experimental data which would support accuracy capability claims for the beam absorption and the storage beam techniques. The last column in Table 4 depicts the projected performance which we consider possible from applying and evaluating the thoughts of Sections 1, 2, and 3 of this paper and from interpreting the experimental data. A comparison between the last two columns of Table 4 gives an approximate idea of the state of knowledge and development of each concept.

6.8. CONCLUSIONS

The (ammonia) travelling beam maser and the (rubidium) optically pumped gas cell have been studied quite extensively and their limitations are well known. The magnitude of the limitations, stated qualitatively in paragraphs (c) and (f) of Section 3, is such that we cannot expect any improvement in the accuracy capability in the foreseeable future as is indicated in Table 4. Their accuracy capability is also, in comparison, so marginal that they are not competitors in the contest for superior primary frequency standards.

The standard with the best accuracy capability at present is the cesium beam tube. The individual effects contributing to this accuracy capability are also comparatively well understood [1—5]. Therefore it is possible to predict that an accuracy capability of 1×10^{-13} may actually be realized in the foreseeable future [1]. The projected performances of the remaining concepts, which are listed in Table 4, are quoted as better than 10^{-12}. Each of the limiting effects for these concepts, as discussed in the corresponding paragraphs of Section 4, has the possibility of being reduced to that level.

How far it will be possible to push beyond 10^{-12} is quite difficult to predict. As a qualitative rule we may state that the magnitude of an error (bias uncertainty) will decrease when the corresponding bias correction is reduced. Also we may gain an advantage when we choose a concept which involves as few bias corrections as possible. Adopting this philosophy we can reexamine those devices listed in Table 4 which hold promise, and we can try to synthesize an optimum solution following the thoughts of Sections 1 to 3. It is evident that no single superior concept can be found. We have to compromise in order to arrive at a practical solution.

In Section 2 we pointed out that a passive technique should be preferred over an active oscillator (maser, laser), although it is difficult to give a fair judgment on all parameters involved. In this paper we are only concerned with "fundamental" limitations and it is conceded that technical and design aspects may well be more important than the fundamental ones. As an example, it remains to be proven experimentally that the detection of a hydrogen beam in the hydrogen storage beam device does not create sufficient technical problems to render its "fundamental" superiority over the hydrogen storage maser ineffective.

In the search for an optimum passive technique the frequency of the transition is an important parameter. A low frequency is of advantage in the interrogation of particles; however, effects caused by particle confinement are fractionally large, and it is necessary to prepare the particles for effective interrogation. The most effective method for particle preparation which also introduces no adverse effects, if proper care is taken, is spatial state selection of a particle beam. For particle confinement at low frequencies we have to rule out simple absorption. Storage in buffer gases introduces large biases and with it relatively large errors. A third method, ion storage, seems to be severely affected by the second order Doppler effect. A significant reduction of this bias (effective ion temperature) appears difficult and its knowledge to correspondingly better than 10^{-13} seems to be a serious problem [50]. Technical difficulties associated with the creation, injection, and preparation of ions may also restrict the usage of ion storage as a method of confinement. However, it should not be considered experimentally impossible, especially if heavy ions are used which reduce adverse heating effects [51].

Two choices are left. The first is the traveling beam method, i.e., in practice an advanced cesium beam tube. The use of particles other than cesium will not give a substantial advantage. The prospects can be fairly well predicted (Table 4). The second choice is the storage beam tube. So far only atomic hydrogen can be stored effectively in a vessel with coated walls. The only limiting effect is the wall interaction (wall shift). At present the wall shift bias is typically of the order of 10^{-11} and can be measured to about 10% [49]. Recent experiments show that the wall shift can actually be made zero at elevated temperatures [52, 53]. We also may assume that bulbs of variable size can be used to evaluate the wall shift with a higher degree of accuracy [54], and that considerably larger storage bulb sizes can be used [55]. If we assume that the wall shift bias could be reduced by one order of magnitude and could be measured to 1% of its value, we would have an accuracy capability of 10^{-14}.

A high frequency transition eliminates most of the problems associated with particle confinement and preparation because we can use simple absorption. Specific problems and technical difficulties may arise in connection with the frequency multiplication and synthesis into the infrared region. We shall assume that these problems can be overcome. Confinement in an absorption cell is possible because the fractional influences of wall and particle collisions are reduced due to the high frequency. Saturated absorption [20] will further reduce adverse effects because only particles with near zero Doppler shift and near zero collisional effects are interrogated. Another choice is the use of a traveling beam [22] which absorbs radiation directed perpendicular to the beam. Effects related to the energy of the interrogating photons, e.g. recoil, can be a limitation which becomes more

pronounced as the transition frequency increases[6] [56].
Existing methods like the methane saturated absorption will allow a study of these effects and will give an indication of how well the bias can be determined or avoided. The fractional difference between the characteristic absorption and emission frequencies due to recoil is theoretically of the order of 10^{-11} for methane.

Following these thoughts one may conclude that such effects are reduced by choosing a transition of lower frequency, e.g., in the far infrared, while still retaining the advantages of a relatively high transition frequency. The optimum frequency for such an approach appears to lie in the lower terahertz region. Here the opportunity for gaining full advantage from techniques based on simple absorption still exists (sufficient population and population difference even at thermal equilibrium, and optical techniques can be used), but the biases related to the energy of the interrogating photons are reduced. These effects can be reduced further and the interrogation time can be increased by using molecules of larger mass. Also the absorption in a traveling beam method should be considered more seriously. Thus accuracy capabilities of better than 10^{-13} may be expected.

In summary we may conclude that among other possibilities the storage beam principle (hydrogen) holds high promise for a quantum electronic frequency standard based on a low (microwave) transition frequency. The other group of techniques which has a potential of competing with or surpassing the projected performance of the cesium beam tube is based on simple absorption in transitions of high frequency, in at least the terahertz region. Both approaches hold the promise for accuracy capabilities of 10^{-14} and are within reach of experimental realization.

6.9. REFERENCES

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